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PHYSICAL AND INORGANIC CHEMISTRY

FOWNES'

MANUAL OF CHEMISTRY

THEORETICAL AND PRACTICAL

VOL. I.

PHYSICAL AND INORGANIC CHEMISTRY

TWELFTH EDITION, REVISED AND CORRECTED

BY HENRY WATTS, B.A., F.R.S.

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PREFACE.

The design of this work is to offer to the student commencing the study of Chemistry an outline of the general principles of that science, and a history of the more important among the very numerous bodies which Chemical Investigations have made known to us. It has no pretensions to be considered a complete treatise on the subject, but is intended to serve as an introduction to the larger and more comprehensive systematic works in our own language and in those of the Continent; and especially to prepare the student for the perusal of original memoirs, which, in conjunction with practical instruction in the laboratory, can alone afford a real acquaintance with the spirit of research and the resources of Chemical Science.

The first three editions were prepared by the Author, the third being nearly completed shortly before his death in January 1849, and published at the beginning of the following year, under the editorship of his friend, the late Dr. H. Bence Jones.

In the six following editions, which were edited by Dr. Bence Jones and Dr. Hofmann, a large amount of new and important matter was added; and in the tenth edition (1868), by Dr. Bence Jones and the present Editor, it was found necessary, in consequence of the rapid advance of the science, and the great changes which had taken place in the entire system of Chemical Philosophy, to make considerable alterations and additions in almost every part of the work.

The chapter on the General Principles of Chemical Philosophy was accordingly re-written; considerable additions were made to the descriptions of the metals, especially those of rarer occurrence; and the distinguishing reactions of the several metals were given more fully than in former editions. The greater part of the Organic Chemistry was also re-written, especially the sections relating to the Hydrocarbons, Alcohols, and Acids, and the compounds belonging to each of these groups were arranged in series.

In the last edition, a considerable amount of new matter was added, chiefly relating to Organic Chemistry; and as these additions are continually increasing, it has been found necessary, in the present edition, to divide the work into two volumes, the first including Chemical Physics and Inorganic Chemistry, and the second being devoted to Organic Chemistry.

The plan adopted by the Author of describing the non-metallic elements and their compounds with one another, before entering upon the discussion of the general principles of Chemical Philosophy, is retained, as the understanding of these General Principles is greatly facilitated by the previous study of a number of special instances of their application; but a short statement of the most important Laws of Chemical Combination, and of the fundamental principles of the Atomic Theory, is given immediately after the description of the compounds of oxygen, in order to introduce the student as soon as possible to the expression of chemical combinations and reactions by Symbolic Notation.

The Weights and Measures used are those of the French Decimal System. Temperatures are expressed in the Centigrade Scale, except where the contrary is stated. A comparative Table of the Centigrade and Fahrenheit Scales is given at the end of the first volume.

HENRY WATTS.

LONDON, *February* 1877.

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A
MANUAL OF CHEMISTRY.

VOL. I.—PHYSICAL AND INORGANIC.

INTRODUCTION.

The Science of Chemistry has for its object the study of the nature and properties of all the materials which enter into the composition or structure of the earth, the sea, and the air, and of the various organised or living beings which inhabit them. Every object accessible to man is thus embraced by the wide circle of Chemical Science.

In ordinary scientific speech the term *chemical* is applied to changes which permanently affect the properties or characters of bodies, in opposition to effects termed *physical,* which are not attended by such consequences. Changes of decomposition or combination are thus easily distinguished from those temporarily brought about by heat, electricity, magnetism, and the attractive forces, whose laws and effects lie within the province of Physics or Natural Philosophy.

Nearly all the objects presented by the visible world are of a compound nature, being chemical compounds, or variously disposed mixtures of chemical compounds, capable of being resolved into simpler forms of matter. Thus, a piece of limestone or marble, by the application of a red heat, is decomposed into quicklime and a gaseous body, carbon dioxide. Both lime and carbon dioxide are in their turn susceptible of decomposition, the former into calcium and oxygen, the latter into carbon and oxygen. For this purpose, however, simple heat does not suffice, the resolution of these substances into their components demanding the exertion of a high degree of chemical energy. Beyond this second step of decomposition the efforts of Chemistry have hitherto been found to fail; and the three bodies, calcium, carbon, and oxygen, having resisted all attempts to resolve them into simpler forms of matter, are accordingly admitted into the list of *elements;* not from an absolute belief in their real oneness of nature, but from the absence of any evidence that they contain more than one description of matter.

The elementary bodies, at present recognised, are sixty-four in number, and about fifty of them belong to the class of *metals.* Several of these are of recent discovery, and are as yet very imperfectly known. The distinction between metals and non-metallic substances, although very convenient for purposes of description, is entirely arbitrary, since the two classes graduate into each other in the most complete manner.

The names of the elements are given in the following table. Opposite to them in the third column are placed certain numbers, which express the proportions in which they combine together, or simple multiples of those proportions; these numbers, for reasons which will be afterwards explained, are called Atomic or Indivisible Weights. In the second column are placed symbols by which these weights are denoted; these symbols are formed of the first letters of the Latin names of the elements, a second letter being added when the names of two or more elements begin with the same letter.

The names of the most important elements are distinguished by the largest and most conspicuous type; those next in importance, by small capitals; while the names of elements which are of rare occurrence, or of which our knowledge is still imperfect, are printed in the ordinary type. The names with an asterisk are those of Non-metallic Elements, the others are names of Metals.

TABLE OF ELEMENTARY BODIES WITH THEIR SYMBOLS AND ATOMIC WEIGHTS.

Name.	Symbol.	Atomic Weight.
ALUMINIUM	Al,	27·4
ANTIMONY (Stibium)	Sb	122
ARSENIC	As	75
BARIUM	Ba	137
Beryllium	Be	9·4
BISMUTH	Bi	210
BORON*	B	11
BROMINE*	Br	80
Cadmium	Cd	112
Cæsium	Cs	133
CALCIUM	Ca	40
CARBON*	C	12
Cerium	Ce	92
CHLORINE*	Cl	35·5
CHROMIUM	Cr	52·2
COBALT	Co	58·8
COPPER (Cuprum)	Cu	63·4
Didymium	D	95
Erbium	E	112·6
FLUORINE*	F	19
Gallium		
GOLD (Aurum)	Au	197
HYDROGEN*	H	1
Indium	In	113·4
IODINE*	I	127
Iridium	Ir	198
IRON (Ferrum)	Fe	56
Lanthanum	La	93·6
LEAD (Plumbum)	Pb	207
Lithium	Li	7
MAGNESIUM	Mg	24
MANGANESE	Mn	55
MERCURY (Hydrargyrum)	Hg	200
Molybdenum	Mo	96
NICKEL	Ni	58·8
Niobium	Nb	94
NITROGEN*	N	14
Osmium	Os	199·2
OXYGEN*	O	16
PALLADIUM	Pd	106·6
PHOSPHORUS*	P	31
PLATINUM	Pt	197·4
POTASSIUM (Kalium)	K	39·1
Rhodium	Rh	104·4
Rubidium	Rb	85·4
Ruthenium	Ru	104·4
Selenium*	Se	79·4
SILICIUM*	Si	28
SILVER (Argentum)	Ag	108
SODIUM (Natrium)	Na	23
STRONTIUM	Sr	87·6
SULPHUR*	S	32
Tantalum	Ta	182
Tellurium*	Te	128
Thallium	Tl	204
Thorinum	Th	235
TIN (Stannum)	Sn	118
Titanium	Ti	50
TUNGSTEN, or Wolfram	W	184
URANIUM	U	240
Vanadium	V	51·2
Yttrium	Y	61·7
ZINC	Zn	65·2
Zirconium	Zr	89·6

It must be distinctly understood that the atomic or combining weights assigned to the elements are merely relative. The number 1 assigned to hydrogen may represent a grain, ounce, pound, gram, kilogram, &c., and the numbers assigned to the other elements will then represent so many grains, ounces, pounds, grams, kilograms, &c. Hydrogen is taken as the unit of the scale, because its combining weight is smaller than that of any other element; but this is merely a matter of convenience; in the older tables of atomic weights that of oxygen was assumed as 100, that of carbon being then 75, that of hydrogen 6·25, &c., &c.

By the combination of the elements in various proportions, and in groups of two, three, or larger numbers, all known compound bodies are produced. And here it is important to state clearly the characters which distinguish true chemical combination from mechanical mixture, and from that kind of adhesion which gives rise to the solution of a solid in a liquid. Bodies may be mixed together in any proportion whatever, the mixture always exhibiting properties intermediate between those of its constituents, and in regular gradation, according to the quantity of each that may be present, as may be seen in the fusion together of metals to form alloys, in the mixture of water with alcohol, of alcohol with ether, and of different oils one with the other. A solid body may also be dissolved in a liquid—salt or sugar in water, for example—in any proportion up to a certain limit, the solution likewise exhibiting a regular gradation of physical properties, according to the quantity of the solid taken up. But a true chemical compound exhibits properties totally different from those of either of its constituent elements, and the proportion of these constituents which form that particular compound admits of no variation whatever. Water, for example, is composed of two elements, oxygen and hydrogen, which, when separated from one another, appear as colourless gases, differing widely in their properties one from the other, and from water in the state of vapour; moreover, water, whether obtained from natural sources, or formed by direct combination of its elements, always contains in 100 parts by weight, 88·9 parts of oyxgen and 11·1 of hydrogen. Common salt, to take another example, is a compound of chlorine and sodium, the former of which, in the separate state, is a yellow gas, the latter a yellowish-white highly lustrous metal, capable of burning in the air, and decomposing water; moreover, from whatever part of the world the salt may be obtained, 100 parts of it invariably contain 39·6 parts of sodium and 60·4 parts of chlorine. Further, when two or more compounds are formed of the same elements, there is no gradual blending of one into the other, as in the case of mixtures, but each compound is sharply defined, and separated, as it were, from the others by an impassable gulf, exhibiting properties distinct from those of the others, and of the elements themselves in the separate state. Thus, there are two compounds of carbon and oxygen, one of which, containing 3 parts by weight of carbon with 4 of oxygen, is an inflammable gas, lighter than atmospheric air, and not absorbed by solution of potash; while the other, which contains 3 parts of carbon and 8 of oxygen, is non-inflammable, heavier than air, and easily absorbed by potash.

Before proceeding with the special description of the several elements and their compounds, it will be convenient to give a short sketch of certain branches of Physical Science, as the physical constitution of Gases, and the chief phenomena of Heat, Light, and Electricity, the partial study of which forms indeed an indispensable Introduction to Chemistry.

PART I.—PHYSICS.

OF DENSITY AND SPECIFIC GRAVITY.

It is of great importance at the outset to understand clearly what is meant by the terms *density* and *specific gravity*. By the *density of a body* is meant its *mass*, or *quantity of matter*, compared with the *mass* or quantity of matter of an *equal volume* of some standard body, arbitrarily chosen. *Specific gravity* denotes the *weight* of a body, as compared with the weight of an equal bulk, or volume, of the standard body, which is reckoned as unity.* In all cases of solids and liquids the standard of unity adopted in this country is with that of water, it is only requisite to weigh equal bulks at the standard temperature, and then divide the weight of the liquid by the weight of the water; the quotient will be greater or less than unity, as the liquid experimented on is heavier or lighter than water. Now, to weigh equal bulks of two fluids, the simplest and best method is clearly to weigh them in succession in the same vessel, taking care that it is equally full on both occasions.

A thin glass bottle, or flask, with a narrow neck, is procured, of the form represented below (fig. 1), and of such capacity as to contain, when filled to about half-way up the neck, exactly 1000 grains of distilled water at 15·5° C. A counterpoise of the exact weight of the empty bottle is made from a bit of brass, an old weight, or something of the kind, and carefully adjusted by filing. The bottle is then graduated, by introducing water at 15·5°, until it exactly balances the 1000-grain weight and counterpoise in the opposite scale; the height at which the water stands in the neck is marked by a scratch, and the instrument is complete for use. The liquid to be examined is brought to the temperature of 15·5°, and with it the bottle is filled up to the mark before mentioned; it is then weighed, the counterpoise being used as before, and the specific gravity directly ascertained.

Fig. 1

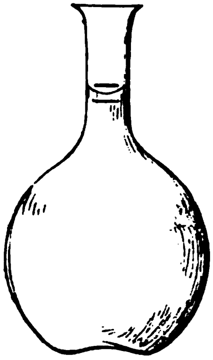
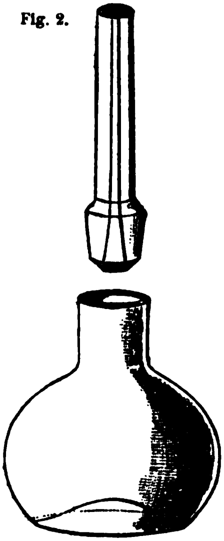


Fig. 2.

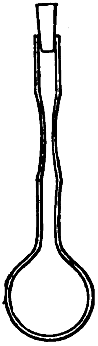


A watery liquid in a narrow glass tube always presents a curved surface, from the molecular action of the glass, the concavity being upwards. It is better, on this account, in graduating the bottle, to make two scratches, as represented in the figure, one at the top and the other at the bottom of the curve. The marks are easily made by a fine, sharp, triangular file, the hard point of which, also, it may be observed, answers perfectly well for writing upon glass, in the absence of a diamond pencil.

It will be quite obvious that the adoption of a flask holding exactly 1000 grains of water has no other object than to save the trouble of a very trifling calculation; any other quantity would answer just as well, and, in fact, the experimental chemist is often compelled to use a bottle of much smaller dimensions, from scarcity of the liquid to be examined.

When the specific gravity of a liquid is to be determined with great accuracy, a case which frequently occurs in chemical inquiries, a little glass bottle is used, of the form shown in fig. 2. This bottle is provided with a perforated conical glass stopper, most accurately fitted by grinding. By completely filling the bottle with liquid, and carefully removing the portion of liquid which is displaced when the stopper is inserted, an unalterable measure is obtained. The least possible quantity of grease applied to the stopper greatly promotes the exact fitting.

Fig. 3.



When the chemist has only a very small quantity of a fluid at his disposal, and wishes not to lose it, the little glass vessel (fig. 3) is particularly useful. It is formed by blowing a bulb on a glass tube. On that portion of the tube which is narrowed by drawing the tube out over a lamp, a fine scratch is made with a diamond. The bulb is filled up to this mark with the liquid whilst it stands in water, the temperature of which is exactly known. A very fine funnel is used for filling the bulb, the stem of the funnel being drawn out so as to enter the tube, and the upper opening of the funnel being small enough to be closed by the finger. The glass stopper is only wanted as a guard, and does not require to fit perfectly.

The determination of the specific gravity of a solid body is made according to the same principles, and may be performed with the specific-gravity bottle (fig. 2). The bottle is first weighed full of water; the solid is then placed in the same pan of the balance, and its weight is determined; finally, the solid is put into the bottle, displacing an equal bulk of water, the weight of which is determined by the loss on again weighing. Thus the weights of the solid and that of an equal bulk of water, are obtained. The former divided by the latter gives the specific gravity.

For example, the weight of a small piece of silver wire was found to be	98·18	grains.
Glass bottle filled with water	294·69	„
	392·87	„
After an equal volume of water was displaced by the silver, the weight was	383·54	„
Hence the displaced water weighed	9·33	„
From this the specific gravity of the silver wire is	$\frac{98{\cdot}18}{9{\cdot}33}=10{\cdot}523$	„

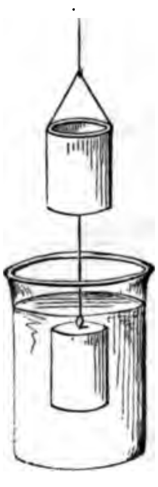
Another highly ingenious, but less exact method of determining the specific gravity of solids, is based on the well-known theorem of Archimedes.

This theorem may be thus expressed:

> When a solid is immersed in a fluid, it loses a portion of its weight; and this portion is equal to the weight of the fluid which it displaces; that is, to the weight of its own bulk of that fluid.

It is easy to give experimental proof of this very important proposition, as well as to establish it by reasoning. Figure 4 represents a little apparatus for the former purpose. This consists of a thin cylindrical vessel of brass, into the interior of which fits very accurately a solid cylinder of the same metal, thus exactly filling it. When the cylinder is suspended beneath the bucket, as seen in the sketch, the whole hung from the arm of a balance and counterpoised, and then the cylinder itself immersed in water, it will be found to have lost a certain weight; and that this loss is precisely equal to the weight of an equal bulk of water, may then be proved by filling the bucket to the brim, whereupon the equilibrium will be restored.

Fig. 4.

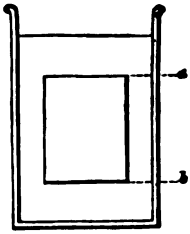


The consideration of the great hydrostatic law of fluid pressure easily proves the truth of the principle laid down. Let the reader figure to himself a vessel of water, having immersed in it a solid cylindrical or rectangular body, and so adjusted with respect to density, that it shall float indifferently in any part beneath the surface (fig. 5).

Now the law of fluid pressure is to this effect:

The pressure exerted by a fluid on any point of the containing vessel, or on any point of a body immersed beneath its surface, is dependent, firstly, upon the density of the fluid, and, secondly, upon the vertical depth of the point in question below the surface. It is independent of the form and lateral dimensions of the vessel or immersed body. Moreover, owing to the peculiar physical constitution of fluids, this pressure is exerted in every direction, upwards, downwards, and laterally, with equal force.

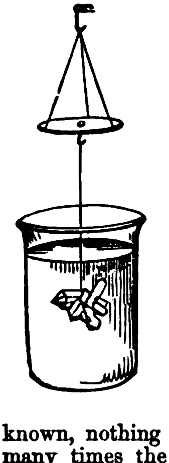
Fig. 5.



The floating body is in a state of equilibrium; therefore the pressure downwards caused by its gravitation must be exactly compensated by the upward transmitted pressure of the column of water *a*, *b*. But this pressure downwards is obviously equal to the weight of an equal quantity of water, since the body of necessity displaces its own bulk. Hence the weight which a body loses when immersed in, or floated on water, is equal to the weight of the volume of water displaced by that body.

Whatever be the density of the substance, it will be buoyed up to this amount; in the case supposed, the buoyancy is equal to the whole weight of the body, which is thus, while in the water, reduced to nothing.

Fig. 6.



A little reflection will show that the same reasoning may be applied to a body of irregular form; besides, a solid of any figure may be divided by the imagination into a multitude of little perpendicular prisms or cylinders, to each of which the argument may be applied. What is true of each individually must necessarily be true of the whole together.

This is the fundamental principle; its application is made in the following manner: Let it be required, for example, to know the specific gravity of a body of extremely irregular form, as a small group of rock crystals: the first part of the operation consists in determining its absolute weight, or, more correctly speaking, its weight in air; it is next suspended from the balance-pan by a fine horsehair, immersed completely in pure water at 15·5°, and again weighed. It now weighs less, the difference being the weight of the water it displaces, that is, the weight of an equal bulk. This being known, nothing more is required than to find, by division, how many times the latter number is contained in the former; the quotient will be the density, water at the temperature of 15·5° being taken = 1. For example :—

The quartz-crystals weigh in air	293·7	grains.
When immersed in water, they weigh . . .	180·1	„
Difference, being the weight of an equal volume of water	113·6	„

$$\frac{293 \cdot 7}{113 \cdot 6} = 2 \cdot 59, \text{ the specific gravity required.}$$

The rule is generally thus written: "Divide the weight in air by the loss of weight in water, and the quotient will be the specific gravity." In reality it is not the weight in air which is required, but the weight the body would have in empty space: the error introduced, namely, the weight of an equal bulk of air, is so trifling, that it is usually neglected.

Sometimes the body to be examined is lighter than water, and floats. In this case, it is first weighed, and afterwards attached to a piece of metal heavy enough to sink it, and suspended from the balance. The whole is then exactly weighed, immersed in water, and again weighed. The difference between the two weighings gives the weight of a quantity of water equal in bulk to both together. The light substance is then detached, and the same operation of weighing in air, and again in water, repeated on the piece of metal. These data give the means of finding the specific gravity, as will be at once seen by the following example:—

Light substance (a piece of wax) weighs in air .	133·7	grains.
Attached to a piece of brass, the whole now weighs	183·7	„
Immersed in water, the system weighs . .	38·8	„
Weight of water equal in bulk to brass and wax	144·9	„
Weight of brass in air	50·0	„
Weight of brass in water	44·4	„
Weight of equal bulk of water	5·6	„
Bulk of water equal to wax and brass . . .	144·9	„
Bulk of water equal to brass alone	5·6	„
Bulk of water equal to wax alone	139·3	„

$$\frac{133 \cdot 7}{139 \cdot 3} = 0 \cdot 9598$$

In all such experiments, it is necessary to pay attention to the temperature and purity of the water, and to remove with great care all adhering air-bubbles;* otherwise a false result will be obtained.

Other cases require mention in which these operations must be modified to meet particular difficulties. One of these happens when the substance is dissolved or acted upon by water. The difficulty is easily overcome by substituting some other liquid of known density which experience shows is without action. Alcohol or oil of turpentine may generally be used when water is inadmissible. Suppose, for instance, the specific gravity of crystallised sugar is required, we proceed in the following way:—The specific gravity of the oil of turpentine is first carefully determined; let it be 0·87; the sugar is next weighed in the air, then suspended by a horsehair, and weighed in the oil; the difference is the weight of an equal bulk of the latter; a simple calculation gives the weight of a corresponding volume of water:—

Weight of sugar in air	400	grains.
Weight of sugar in oil of turpentine . .	182·5	„
Weight of equal bulk of oil of turpentine	217·5	„

87 : 100 = 217·5 : 250,

the weight of an equal bulk of water: hence the specific gravity of the sugar,—

$$\frac{400}{250} = 1·6 .$$

If the substance to be examined consists of small pieces, or of powder, the method first described, namely, that of the specific gravity bottle, can alone be used.

By this method the specific gravities of metals in powder, metallic oxides, and other compounds, and salts of all descriptions, may be determined with great ease. Oil of turpentine may be used with most soluble salts. The crystals should be crushed or roughly powdered to avoid errors arising from cavities in their substance.

The specific gravity of a solid can also be readily found by immersing it in a transparent liquid, the density of which has been so adjusted that the solid body remains indifferently at whatever depth it may be placed. The specific gravity of the liquid must now be determined, and it will, of course, be the same as that of the solid. It is necessary that the liquid chosen for this experiment do not dissolve or in any way act upon the solid. Solutions of mercuric nitrate, or corrosive sublimate, can be used for bodies heavier than water, whilst certain oils, and essences, and mixtures of alcohol and water, can be conveniently employed for such substances as have a lower specific gravity than water. This method is not only adapted to the exact determination of specific gravities, but also serves in many cases as a means of readily distinguishing substances much resembling one another. Suppose, for instance, a solution of mercuric nitrate to have a specific gravity 3; a red amethyst (2·67) will then float upon, and a topaz of the same colour (3·55) will sink in this liquid.

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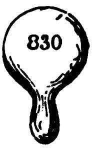
* A simple plan of avoiding altogether the adhesion of air-bubbles, which often are not easily perceived, consists in heating the water to ebullition, introducing the body which has been weighed in the air into the still boiling water, which is then allowed to cool to 15·5°, when the second weighing is performed.

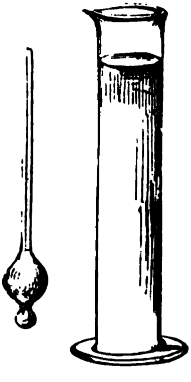
Hydrometers.—The theorem of Archimedes affords the key to the general doctrineof the equilibrium of floating bodies, of which an application is made in the common hydrometer,—an instrument for finding the specific gravities of liquids in a very easy and expeditious manner.

Fig. 7.



When a solid body is placed upon the surface of a liquid specifically heavier than itself, it sinks down until it displaces a quantity of liquid equal to its own weight, at which point it floats. Thus, in the case of a substance floating in water, whose specific weight is one-half that of the liquid, the position of equilibrium will involve the immersion of exactly one-half of the body, inasmuch as its whole weight is counterpoised by a quantity of water equal to half its volume. If the same body were put into a liquid of one-half the specific gravity of water, if such could be found, it would then sink beneath the surface, and remain indifferently in any part. A floating body of known specific gravity may thus be used as an indicator of the specific gravity of a liquid. In this manner little glass beads (fig. 7) of known specific gravities are sometimes employed in the arts to ascertain in a rude manner the specific gravity of liquids; the one that floats indifferently beneath the surface, without either sinking or rising, has of course the same specific gravity as the liquid itself; this is pointed out by the number marked upon the bead.

Fig. 8.



The hydrometer (fig. 8) in general use consists of a floating vessel of thin metal or glass, having a weight beneath to maintain it in an upright position, and a stem above bearing a divided scale. The use of the instrument is very simple. The liquid to be tried is put into a small narrow jar, and the instrument floated in it. It is obvious that the denser the liquid, the higher will the hydrometer float, because a smaller displacement of liquid will counterbalance its weight. For the same reason, in a liquid of less density, it sinks deeper. The hydrometer comes to rest almost immediately, and then the mark on the stem at the fluid-level may be read off.

Very extensive use is made of instruments of this kind in the arts: they sometimes bear different names, according to the kind of liquid for which they are intended; but the principle is the same in all. The graduation is very commonly arbitrary, two or three different scales being unfortunately used. These may be sometimes reduced, however, to the true numbers expressing the specific gravity by the aid of tables of comparison drawn up for the purpose. (*See* APPENDIX.) Tables are likewise used to reduce the readings of the hydrometer at any temperature to those of the normal temperature.

It is much better, however, to use a hydrometer having the true scale of specific gravities marked upon its stem. To graduate such an instrument, a sufficient number of standard points may be determined by immersing it in liquids of known specific gravity, and the small intervals between these points divided into equal parts.*

The determination of the specific gravity of gases and vapours of volatile liquids is a problem of very great practical importance to the chemist: the theory of the operation is as simple as when liquids themselves are concerned, but the processes are much more delicate, and involve besides certain corrections for differences of temperature and pressure, founded on principles yet to be discussed. It will be proper to defer the consideration of these matters for the present.

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* For an accurate method of dividing the hydrometer scale when only a few points are determined by actual observation, see the article "Hydrometer," by Professor Jevons, in Watts's *Dictionary of Chemistry*, vol. iii. p. 206.

THE PHYSICAL CONSTITUTION OF THE ATMOSPHERE, AND OF GASES IN GENERAL.

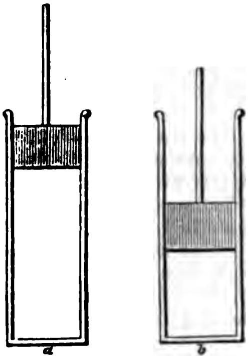
It requires some little abstraction of mind to realise completely the condition in which all things at the surface of the earth exist. We live at the bottom of an immense ocean of gaseous matter, which envelopes everything, and presses upon everything with a force which appears, at first sight, perfectly incredible, but whose actual amount admits of easy proof.

Gravity being, so far as is known, common to all matter, it is natural to expect that gases, being material substances, should be acted upon by the earth's attraction, as well as solids and liquids. This is really the case, and the result is the weight or pressure of the atmosphere, which is nothing more than the effect of the attraction of the earth on the particles of air.

Before describing the leading phenomena of the atmospheric pressure, it is necessary to notice one very remarkable feature in the physical constitution of gases, upon which depends the principle of the air-pump.

Gases are in the highest degree elastic; the volume or space which a gas occupies depends upon the pressure exerted upon it. Let the reader imagine a cylinder, *a*, closed at the bottom, in which moves a piston air-tight, so that no air can escape between the piston and the cylinder. Suppose now the piston be pressed downwards with a certain force; the air beneath it will be compressed into a smaller bulk, the amount of this compression depending on the force applied; if the power be sufficient, the bulk of the gas may be thus diminished to one hundredth part or less. When the pressure is removed, the elasticity or *tension*, as it is called, of the included air or gas, will immediately force up the piston until it arrives at its first position.

Fig. 9.



Again, take fig. 9, *b*, and suppose the piston to stand about the middle of the cylinder, having air beneath in its usual state. If the piston be now drawn upwards, the air below will expand, so as to fill completely the increased space, and this to an apparently unlimited extent. A volume of air, which, under ordinary circumstances, occupies the bulk of a cubic inch, might, by the removal of the pressure upon it, be made to expand to the capacity of a whole room, while a renewal of the former pressure would be attended by a shrinking down of the air to its former bulk. The smallest portion of gas introduced into a large exhausted vessel becomes at once diffused through the whole space, an equal quantity being present in every part; the vessel is *full* although the gas is in a state of extreme tenuity. This power of expansion which air possesses may have, and probably has, in reality, a limit; but the limit is never reached in practice. We are quite safe in the assumption, that for all purposes of experiment, however refined, air is perfectly elastic.

It is usual to assign a reason for this indefinite expansibility by ascribing to the particles of material bodies, when in a gaseous state, a self-repulsive agency. The statement is commonly made somewhat in this manner: matter is under the influence of two opposite forces, one of which tends to draw the particles together, the other to separate them. By the preponderance of one or other of these forces, we have the three states called solid, liquid, and gaseous. When the particles of matter, in consequence of the direction and strength of their mutual attractions, possess only a very slight power of motion, a solid substance results; when the forces are nearly balanced, we have a liquid, the particles of which in the interior of the mass are free to move, but yet to a certain extent are held together; and, lastly, when the attractive power seems to be completely overcome by its antagonist, we have a gas or vapour.

forces open the upper valve, and escapes into the atmosphere In this manner a cylinder full of air is removed from the receiver at every stroke of the pump. During the descent of the piston, the upper valve remains open, and the lower closed, and the reverse during the opposite movement.

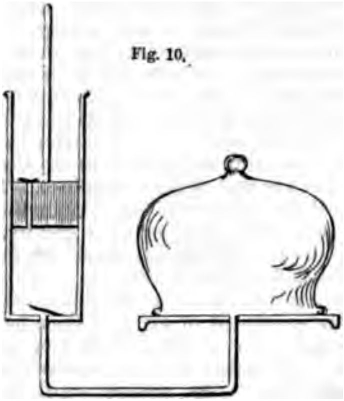


Fig. 10.

In practice, it is very convenient to have two such barrels or cylinders, arranged side by side, the piston-rods of which are formed into racks, having a pinion or small-toothed wheel between them, moved by a winch. By this contrivance the operation of

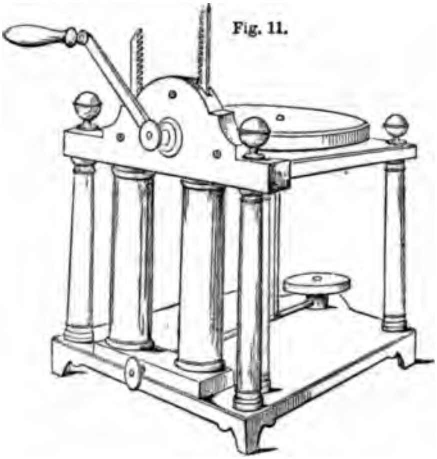
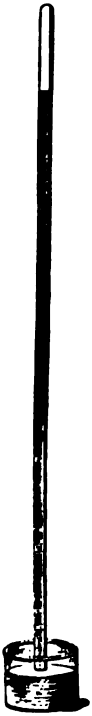


Fig. 11.

exhaustion is much facilitated, and the labour lessened. The arrangement is shown in fig. 11.

Atmospheric Pressure—The Barometer.—Air has weight; a light flask or globe of glass, furnished with a stop-cock and exhausted by the air-pump, weighs considerably less than when full of air. If the capacity of the vessel be equal to 100 cubic inches, this difference may amount to nearly 30 grains.

Fig. 12.



After what has been said on the subject of fluid pressure, it will scarcely be necessary to observe that the law of equality of pressure in all directions also holds good in the case of the atmosphere. The perfect mobility of the particles of air permits the transmission of the force generated by their gravity. The sides and bottom of an exhausted vessel are pressed upon with as much force as the top.

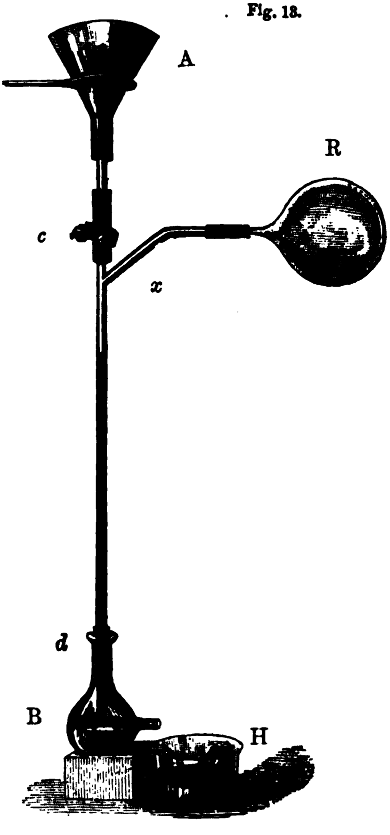
If a glass tube of considerable length could be perfectly exhausted of air, and then held in an upright position, with one of its ends dipping into a vessel of liquid, the latter, on being allowed access to the tube, would rise in its interior until the weight of the column balanced the pressure of the air upon the surface of the liquid. Now, if the density of this liquid were known, and the height and area of the column measured, means would be furnished for exactly estimating the amount of pressure exerted by the atmosphere. Such an instrument is the barometer. To construct it, a straight glass tube, 36 inches long, is sealed by the blowpipe flame at one end; it is then filled with clean, dry mercury, care being taken to displace all air-bubbles, the open end stopped with a finger, and the tube inverted in a basin of mercury. On removing the finger, the mercury falls away from the top of the tube, until it stands at the height of about 30 inches above the level of that in the basin. Here it remains supported by, and balancing the atmospheric pressure, the space above the mercury in the tube being of necessity empty.

The pressure of the atmosphere is thus seen to be capable of sustaining a column of mercury 30 inches in height, or thereabouts. Now such a column, having an area of 1 inch, weighs between 14 and 15 lbs.; consequently such must be the amount of the pressure exerted upon every square inch of the surface of the earth, and of the objects situated thereon, at least near the level of the sea. This enormous force is borne without inconvenience by the animal frame, by reason of its perfect uniformity in every direction; and it may be doubled, or even tripled, without injury.

A barometer may be constructed with other liquids besides [illegible]rcury; but, as the height of the column must always bear an inverse proportion to the density of the liquid, the length of tube required will be often considerable; in the case of water it will exceed 33 feet. It is seldom that any other liquid than mercury is employed in the construction of this instrument. The Royal Society of London possessed a water barometer at their apartments at Somerset House. Its construction was attended with great difficulties, and it was found impossible to keep it in repair.

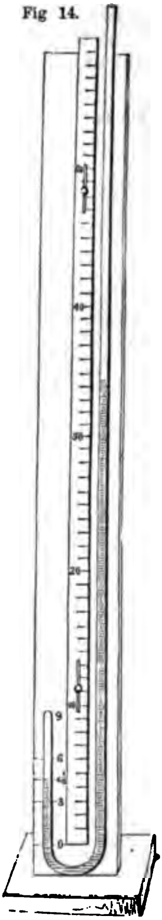
Sprengel's Air-pump.—If an aperture be made in the top of a barometer tube, the mercury will sink, and draw in air; and if the experiment be so arranged as to allow air to enter along with the mercury, and the supply of air is limited, while that of the mercury is unlimited, the air will be carried away and a vacuum produced. On this principle, Dr Sprengel has contrived an apparatus by which a very complete exhaustion may be obtained. *cd* (fig. 13), is a glass tube longer than a barometer, open at both ends, and connected, by means of india-rubber tubing, with a funnel A filled with mercury, and supported on a stand. Mercury is allowed to fall through this tube at a rate regulated by a clamp at *c;* the lower end of the tube *cd* fits into the flask B, which has a spout at its side, a little higher than the lower end of the tube *cd;* the upper part of this tube has a branch at *x*, to which a receiver R can be tightly fixed. When the clamp at *c* is opened, the first portion of mercury that runs out closes the tube and prevents it from entering below. As the mercury is allowed to run down, the exhaustion begins, and the whole length of the tube from *x* to *d* is filled with

Fig. 13.



cylinders of air and mercury having a downward motion. Air and mercury escape through the spout of the bulb B, below which is placed a basin H to receive the mercury; and this mercury is poured back from time to time into the funnel A, to be repassed through the tube till the exhaustion is complete. As this point is approached, the enclosed air between the mercury-cylinders is seen to diminish, until the lower part of *cd* forms a continuous column of mercury about 30 inches high. The operation is complete when the column of mercury is quite free from air, and a drop of mercury falls on the top of it without enclosing the smallest air-bubble. The height of the column is then equal to that of the mercury in the barometer; in other words, the apparatus is a barometer whose vacuum is the receiver R. It may be advantageously combined with an exhausting syringe, which removes the greater part of the air, the exhaustion being then completed as above.

Fig 14.



Relations between Pressure, Elasticity, and Volume of Gases.—It will now be necessary to consider a most important law which connects the volume occupied by a gas with the pressure made upon it, and is thus expressed:—

The volume of gas is *inversely* as the pressure; the density and elastic force are *directly* as the pressure, and *inversely* as the volume.

For instance, 100 cubic inches of gas under a pressure of 30 inches of mercury would expand to 200 cubic inches were the pressure reduced to one-half, and shrink, on the contrary, to 50 cubic inches if the original pressure were doubled. The change of density must necessarily be in the inverse proportion to that of the volume, and the elastic force follows the same rule.

This, which is usually called the law of Mariotte, though really discovered by Boyle (1661), is easily demonstrable by direct experiment. A glass tube (fig. 14), about 7 feet long, is closed at one end, and bent into the form represented in fig. 14, the open limb of the syphon being the longer. It is next attached to a board furnished with a movable scale of inches, and enough mercury is introduced to fill the bend, the level being evenly adjusted, and marked upon the board. Mercury is now poured into the tube until the enclosed air is reduced to one-half of its former volume; and on applying the scale, it will be found that the level of the mercury in the open part of the tube stands very nearly 30 inches above that in the closed portion. The pressure of an additional "atmosphere" has consequently reduced the bulk of the contained air to one-half. If the experiment be still continued until the volume of air is reduced to a third, it will be found that the column measures 60 inches, and so in like proportion as far as the experiment is carried.

The above instrument is better adapted for illustration of the principle than for furnishing rigorous proof of the law. This has, however, been done. MM. Arago and Dulong published, in the year 1830, an account of certain experiments made by them in Paris, in which the law in question had been verified to the extent of twenty-seven atmospheres. With rarefied air also, of whatever degree of rarefaction, the law has been found true.

All gases are alike subject to this law, and all vapours of volatile liquids, when remote from their points of liquefaction.* It is a matter of the greatest importance in practical chemistry, since it gives the means of making corrections for pressure, or determining by calculation the change of volume which a gas would suffer by any given change of external pressure.

Let it be required, for example, to solve the following problem We have 100 cubic inches of gas in a graduated jar, the barometer standing at 29 inches; how many cubic inches will it occupy when the column rises to 30 inches? Now the volume must be inversely as the pressure: consequently a change of pressure in the proportion of 29 to 30 must be accompanied by a change of volume in the proportion of 30 to 29, the 30 cubic inches of gas contracting to 29 cubic inches under the conditions imagined Hence the answer—

$$30 : 29 = 100 : 96{\cdot}67 \text{ cubic inches.}$$

The reverse of the operation will be obvious. The pupil will do well to familiarise himself with the simple calculations of correction for pressure.

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* Near the liquefying point the law no longer holds; the volume diminishes *more rapidly* than the theory indicates, a smaller amount of pressure being hen sufficient. (See further, p. 50).

HEAT.

It will be convenient to consider the subject of heat under several sections, and in the following order:—

1. Expansion of bodies, or effects of variations of temperature in altering their dimensions.
2. Conduction, or transmission of heat.
3. Specific heat.
4. Change of state.
5. Sources of heat.
6. Dynamical theory of heat.

Expansion.

If a bar of metal of such magnitude as to fit accurately to a gauge, when cold, be heated considerably, and again applied to the gauge, it will be found to have become enlarged in all its dimensions. When cold, it will once more enter the gauge.

Again, if a quantity of liquid contained in a glass bulb furnished with a narrow neck, be plunged into hot water, or exposed to any other source of heat, the liquid will mount in the stem, showing that its volume has been increased. The bulb, however, has likewise expanded by the heat, and its capacity has consequently been augmented. The rise of the liquid in the tube, therefore, denotes the difference between these two expansions.

Fig. 15.

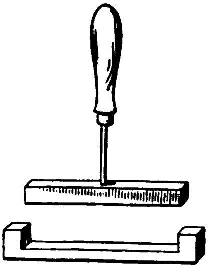


Fig. 16.

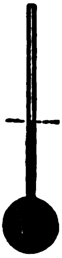
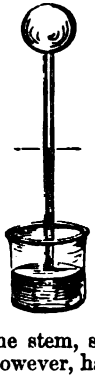


Fig. 17.

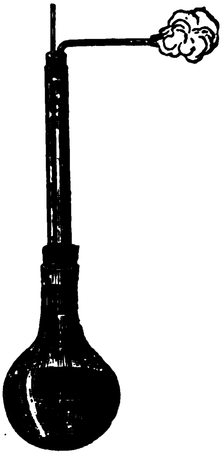


Or, if a portion of air be confined in any vessel, the application of a slight degree of heat will suffice to make it occupy a space sensibly larger.

This most general of all the effects of heat furnishes in the outset a principle, by the aid of which an instrument can be constructed capable of taking cognisance of changes of temperature in a manner equally accurate and convenient: such an instrument is the thermometer.

A capillary glass tube is chosen, of uniform diameter; one extremity is closed and expanded into a bulb, by the aid of the blowpipe flame, and the other somewhat drawn out, and left open. The bulb is now cautiously heated by a spirit-lamp, and the open extremity plunged into a vessel of mercury, a portion of which rises into the bulb when the latter cools, replacing the air which had been expanded and driven out by the heat. By again applying the flame, and causing this mercury to boil, the remainder of the air is easily expelled, and the whole space filled with mercurial vapour. The open end of the tube must now be immediately plunged into the vessel filled with mercury. As the metallic vapours condense, the pressure of the external air forces the liquid metal into the instrument, until finally the tube is completely filled with mercury. The thermometer thus filled is now to be heated until so much mercury has been driven out by the expansion of the remainder, that its level in the tube shall stand at common temperatures at the point required. This being satisfactorily adjusted, the heat is once more applied, until the column rises quite to the top; and then the extremity of the tube is hermetically sealed by the blowpipe. The retraction of the mercury on cooling now leaves an empty space, which is essential to the perfection of the instrument.

Fig. 18.



The thermometer has yet to be graduated; and to make its indications comparable with those of other instruments, a scale, having at the least two fixed points, must be adapted to it.

It has been observed, that the temperature of melting ice, that is to say, of a mixture of ice and water, is always constant; a thermometer, already graduated, plunged into such a mixture, always marks the same degree of temperature, and a simple tube filled in the manner described and so treated, exhibits the same effect in the unchanged height of the little mercurial column, when tried from day to day. The freezing point of water, or melting point of ice, constitutes then one of the invariable temperatures demanded.

Another is to be found in the boiling point of water, or, more accurately, in the temperature of steam which rises from boiling water. In order to give this temperature, which remains perfectly constant whilst the barometric pressure is constant, to the mercury of the thermometer, distilled water is made to boil in a glass vessel with a long neck, when the pressure is at 30 inches (fig. 17). The thermometer is then so placed that all the mercury is surrounded with steam. It quickly rises to a fixed point, and there it remains as long as the water boils, and the height of the barometer is unchanged.

The tube having been carefully marked with a file at these two points, it remains to divide the interval into degrees: this division is entirely arbitrary. The scale now most generally employed is the Centigrade, in which the space is divided into 100 parts, the zero being placed at the freezing point of water. The scale is continued above and below these points, numbers below 0 being distinguished by the negative sign.

In England the division of Fahrenheit is still in use: the above mentioned space is divided into 180 degrees; but the zero, instead of starting from the freezing point of water, is placed 32 degrees below it, so that the temperature of ebullition is expressed by 212°.

The plan of Reaumur is nearly confined to a few places in the north of Germany and to Russia: in this scale the freezing point of water is made 0°, and the boiling point 80°.

It is unfortunate that a uniform system has not been generally adopted in graduating thermometers: this would render unnecessary the labour which now so frequently has to be performed of translating the language of one scale into that of another. To effect this, presents, however, no great difficulty. Let it be required, for example, to know the degree of Fahrenheit's scale which corresponds to 60° C.

$$100^\circ \text{ C.} = 180^\circ \text{ F.}; \text{ or } 5^\circ \text{ C.} = 9^\circ \text{ F.}$$

Consequently,

$$5 : 9 = 60 : 108.$$

But then, as Fahrenheit's scale commences with 32° instead of 0°, that number must be added to the result, making 60° C. = 140° F.

The rule, then, is the following:—To convert centigrade degrees into Fahrenheit degrees, multiply by 9, divide the product by 5, and add 32; to convert Fahrenheit degrees into centigrade degrees, subtract 32, multiply by 5, and divide by 9.

The reduction of negative degrees, or those below zero of one scale into those of another scale, is effected in the same way. For example, to convert − 15° C. into degrees of Fahrenheit, we have—

$$-15 \times \frac{9}{5} + 32 = -27 + 32 = +5 \text{ F.}$$

In this work temperatures will always be given in centigrade degrees, unless the contrary is stated.

Mercury is usually chosen for making thermometers, on account of its regularity of expansion within certain limits, and because it is easy to have the scale of great extent, from the large interval between the freezing and boiling points of the metal. Other substances are sometimes used; alcohol is employed for estimating very low temperatures, because this liquid has not been frozen even at the lowest degree of cold which has been artificially produced.

Air-thermometers are also used for some few particular purposes; indeed, the first thermometer ever made was of this kind. There are two modifications of this instrument: in the first, the liquid into which the tube dips is open to the air; and in the second, shown in fig. 19, the atmosphere is completely excluded. The effects of expansion are in the one case complicated with those arising from changes of pressure, and in the other they cease to be visible at all when the *whole* instrument is subjected to alterations of temperature, because the air in the upper and lower reservoir, being equally affected by such changes, no alteration in the height of the fluid column can occur. Accordingly, such instruments are called *differential* thermometers, since they serve to measure differences of temperature between the two portions of air, while changes affecting both alike are not indicated. Fig. 20 shows another form of the same instrument.

Fig. 19.

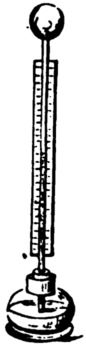
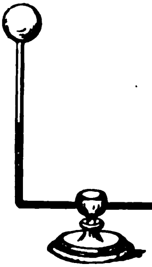


Fig. 20.



The air-thermometer may be employed for measuring all temperatures from the lowest to the highest; M. Pouillet has described one by which the heat of an air-furnace could be measured. The reservoir of this instrument is of platinum, and it is connected with a piece of apparatus by which the increase of volume experienced by the included air is determined.

An excellent air-thermometer has been constructed and used by Rudberg, and more recently by Magnus and Regnault, for measuring the expansion of the air. Its construction depends on the law, that when air is heated and hindered from expanding, its tension increases in the same proportion in which it would have increased in volume if permitted to expand.

All bodies are enlarged by the application of heat, and reduced by its abstraction, or, in other words, contracted on being artificially cooled. This effect takes place to a comparatively small extent with solids, to a larger amount in liquids, and most of all in the case of gases.

Each solid and liquid has a rate of expansion peculiar to itself; gases, on the contrary, expand nearly alike for the same increase of heat.

Expansion of Solids.—The actual amount of expansion which different solids undergo by the same increase of heat has been carefully investigated. The following are some of the results of the best investigations, more particularly those of Lavoisier and Laplace. The fraction indicates the amount of expansion in length suffered by the rods of the undermentioned bodies in passing from 0° to 100°:—

Fir-wood*	[illegible]	Tempered steel	[illegible]
English flint glass	[illegible]	Soft iron	[illegible]
Platinum	[illegible]	Gold	[illegible]
Common white glass	[illegible]	Copper	[illegible]
Common white glass	[illegible]	Brass	[illegible]
Glass without lead	[illegible]	Silver	[illegible]
Another specimen	[illegible]	Lead	[illegible]
Steel untempered	[illegible]	Zinc	[illegible]

From the linear expansion, the cubic expansion, or measure of volume, may be calculated. When the expansion of a body in different directions is equal, as for example in glass, hammered metals, and generally in most uncrystallised substances, it will be sufficient to triple the fraction expressing the increase in one dimension. This rule does not hold good for crystals belonging to irregular systems, for they expand unequally in the direction of the different axes.

Metals appear to expand pretty uniformly for equal increments of heat within the limits stated; but above the boiling point of water the rate of expansion becomes irregular and more rapid.

The force exerted in the act of expansion is very great. In laying down railways, building iron bridges, erecting long ranges of steam-pipes, and in executing all works of the kind in which metal is largely used, it is indispensable to make provision for these changes of dimensions.

In consequence of glass and platinum having nearly the same amount of expansion, a thin platinum wire may be fused into a glass tube, without any fear that the glass will break on cooling.

A very useful application of expansion by heat is that of the cutting of glass by a hot iron; this is constantly practised in the laboratory for a great variety of purposes. The glass to be cut is marked with ink in the required direction, and then a crack, commenced by any convenient method, at some distance from the desired line of fracture, may be led by the point of a heated iron rod along the latter with the greatest precision.

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* In the direction of the vessels.

Expansion of Liquids.—The dilatation of a liquid may be determined by filling a thermometer with it, in which the relation between the capacity of the ball and that of the stem is exactly known, and observing the height of the column at different temperatures. It is necessary in this experiment to take into account the effects of the expansion of the glass itself, the observed result being evidently the *difference* of the two.

Liquids vary exceedingly in this particular. The following table is taken from Péclet's "Éléments de Physique:"—

Apparent Dilatation in Glass between 0° *and* 100°.

Water,	$\frac{1}{23}$
Hydrochloric acid, sp. gr. 1·137,	$\frac{1}{27}$
Nitric acid, sp. gr. 1·4,	$\frac{1}{9}$
Sulphuric acid, sp. gr. 1·85,	$\frac{1}{17}$
Ether,	$\frac{1}{14}$
Olive oil,	$\frac{1}{12}$
Alcohol,	$\frac{1}{9}$
Mercury,	$\frac{1}{65}$

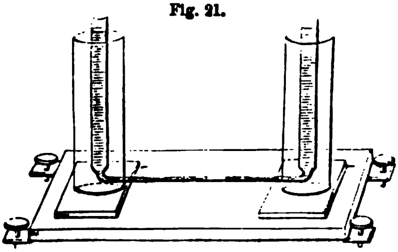
Most of these numbers must be taken as representing mean results; for there are few liquids, which, like mercury, expand regularly between these temperatures. Even mercury above 100° shows an unequal and increasing expansion, if the temperature indicated by the air-thermometer be used for comparison. This is shown by the following abstract of a table given by Regnault:—

Reading of Air Thermometer.	Reading of Mercurial Thermometer.	Temperature deduced from the Absolute Expansion of Mercury.
0°	0°	0°
100°	100°	100°
200°	200°	202·78°
300°	301°	308·34°
350°	354°	362·16°

The absolute amount of expansion of mercury is, for many reasons, a point of great importance; it has been very carefully determined by a method independent of the expansion of the containing vessel. The apparatus employed for this purpose, first by Dulong and Petit, and later by Regnault, is shown in fig. 21, divested, however, of many of its subordinate parts. It consists of two upright glass tubes, connected at their bases by a horizontal tube of much smaller dimensions. Since a free communication exists between the two tubes, mercury poured into the one will rise to the same level in the other, provided its temperature is the same in both tubes; when this is not the case, the hotter column will be the taller, because the expansion of the metal diminishes its specific gravity, and the law of hydrostatic equilibrium requires that the height of such columns should be inversely as their densities. By the aid of the outer cylinders, one of the tubes is maintained constantly at 0°, while the other is raised, by means of heated water or oil, to any required temperature. The perpendicular height of the columns may then be read off by a horizontal micrometer telescope, moving on a vertical divided scale.

These heights represent volumes of equal weight, because volumes of equal weight bear an inverse proportion to the densities of the liquids, so that the amount of expansion admits of being very easily calculated. Thus, let the column at 0° be 6 inches high, and that at 100°, 6·108 inches; the increase of height, 108 on 6000, or $\frac{1}{55\cdot5}$ part of the whole, will represent the absolute cubical expansion.

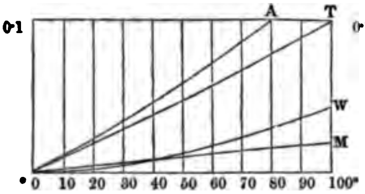
Fig. 21.



The indications of the mercurial thermometer are inaccurate when very high ranges of temperature are concerned, from the increased expansibility of the metal. The error thus caused is, however, nearly compensated, for temperatures under 204·5°, by the expansion of the glass tube. For higher temperatures a small correction is necessary, as the above table shows.

To what extent the expansion of different liquids may vary between the same temperatures is obvious from a glance at fig. 22

Fig. 22.



which represents the expansion of mercury (M), water (W), oil of turpentine (T), and alcohol (A). A column of these several liquids, equalling at 0° the tenfold height of the line 0 0·1 in the diagram, would exhibit, when heated to a temperature of 10°, 20°, 30°, &c., an expansion indicated by the distances at which the perpendicular lines drawn over the numbers 10, 20, 30, &c., are intersected by the curves belonging to each of these liquids. Thus it is seen that oil of turpentine, between 0° and 100°, expands very nearly $\frac{1}{10}$ of its volume, and that mercury between the same limits of temperature expands uniformly, while the rate of expansion of the other liquids increases with the rise of the temperature.

An exception to the regularity of expansion in liquids exists in the case of water; it is so remarkable, and its consequences so important, that it is necessary to advert to it particularly.

Let a large thermometer-tube be filled with water at the common temperature of the air, and then artificially cooled. The liquid will be observed to contract, until the temperature falls to about 4° C. (39·2° F., or 7·2° above the freezing point.) After this a further reduction of temperature causes expansion instead of contraction in the volume of the water, and this expansion continues until the liquid arrives at its point of congelation, when so sudden and violent an enlargement takes place that the vessel is almost invariably broken. At the temperature of 4° water is at its maximum density; increase or diminution of heat produces upon it, for a short time, the same effect.

According to the latest researches of Kopp, the point of greatest density of water is 4·08° C. (39·34° F.) According to the determinations of this physicist, the volume of water = 1 at 0° C. changes, when heated, to the following volumes:—

2°	0·99991	16°	1·00085	35°	1·00570	70°	1·02225
4°	0·99988	18°	1·00118	40°	1·00753	75°	1·02544
6°	0·99990	20°	1·00157	45°	1·00954	80°	1·02858
8°	0·99999	22°	1·00200	50°	1·01177	85°	1·03189
10°	1·00012	24°	1·00247	55°	1·01410	90°	1·03540
12°	1·00031	25°	1·00272	60°	0·01659	95°	1·03909
14°	1·00056	30°	1·00406	65°	1·01930	100°	1·04299

Sea-water has no point of maximum density above the freezing point. The more it is cooled the denser it becomes, until it solidifies at −2·6°.

The gradual expansion of pure water cooled below 4° must be carefully distinguished from the great and sudden increase of volume it exhibits in the act of freezing, in which respect it resembles many other bodies which expand on solidifying. The force thus exerted by freezing water is enormous. Thick iron shells quite filled with water, and exposed with their fuse-holes securely plugged, to the cold of a Canadian winter night, have been found split on the following morning. The freezing of water in the joints and crevices of rocks is a most potent agent in their disintegration.

Expansion of Gases.—The principal laws relating to the expansion of gases are contained in the four following propositions:—

1. All gases expand nearly alike for equal increments of heat; and all vapours, when remote from their condensing points, follow the same law.
2. The rate of expansion is not altered by a change in the state of compression, or elastic force, of the gas itself.
3. The rate of expansion is uniform for all degrees of heat.
4. The actual amount of expansion is equal to $\frac{1}{273}$ or $\frac{11}{3000}$ or 0·003666 of the volume of the gas at 0° centigrade, for each degree of the same scale.*

It will not be necessary to enter into any description of the methods of investigation by which these results have been obtained; the advanced student will find in Pouillet's "Eléments de Physique," and in the papers of Magnus and Regnault,† all the information he may require.

In the practical manipulation of gases, it very often becomes necessary to make a correction for temperature, or to discover how much the volume of a gas would be increased or diminished by a particular change of temperature; this can be effected with great facility. Let it be required, for example, to find the volume which 100 cubic inches of any gas at 10° would become on the temperature rising to 20°.

The rate of expansion is $\frac{1}{273}$ or $\frac{11}{3000}$ of the volume at 0° for each degree; or 3000 measures at 0° become 3011 at 1°, 3022 at 2°, 3110 at 10°, and 3220 at 20°. Hence

Meas. at 10°.		Meas. at 20°.		Meas. at 10°.		Meas. at 20°.
3110	:	3220	=	100	:	103·537.

If this calculation is required to be made on the Fahrenheit scale, it must be remembered that the zero of that scale is 32° below the melting-point of ice. Above this temperature the expansion for each degree of the Fahrenheit scale is $\frac{1}{480}$ of the original volume.

This, and the correction for pressure, are operations of very frequent occurrence in chemical investigations, and the student will do well to become familiar with them.

The following formula includes both these corrections:—Let V and V′ be the volume of a gas at the temperatures t and t' centigrade, and under the pressures p and p', measured in millimeters of mercury: then

$$\frac{V}{V'} = \frac{1 + 0{\cdot}003666t}{1 + 0{\cdot}003666t'} \quad \frac{p'}{p}$$

The case which most frequently occurs is the reduction of a

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[*] The fraction $\frac{11}{3000}$ is very convenient for calculation.

[†] Poggendorff's Annalen, iv. 1—Ann. Chim. Phys. 3d series, iv. 5, and v. 52. See also Watts's Dictionary of Chemistry, art. Heat, vol. iii. p. 46; and Ganot's Eléments de Physique, translated by Dr Atkinson, 4th edition, pp. 253–262.

measured volume, V, of a gas at the temperature t and pressure p to the volume V_0, which it would occupy at 0° C., and under a pressure of 760 mm. In this case, we have $t'=0$, and $p'=760$, therefore

$$\frac{V}{V_0} = (1+0{\cdot}003666t)\,.\,\frac{760}{p}\,,$$

and

$$V_0 = \frac{V}{1+0{\cdot}003666t}\,.\,\frac{p}{760}\,.$$

If the barometric pressure is measured in inches, the number 30 must be substituted for 760.

Note.—Of the four propositions stated in the text, the first and second have recently been shown to be true within certain limits only; and the third, although in the highest degree probable, would be very difficult to demonstrate rigidly; in fact, the equal rate of expansion of air is assumed in all experiments on other substances, and becomes the standard by which the results are measured.

The rate of expansion for the different gases is *not* absolutely the same, but the difference is so small that for most purposes it may safely be neglected. Neither is the state of elasticity altogether indifferent, the expansion being sensibly *greater* for an equal rise of temperature when the gas is in a compressed state.

It is important to notice that the greatest deviations from the rule are exhibited by those gases which, as will hereafter be seen, are most easily liquefied, such as carbon dioxide, cyanogen, and sulphur dioxide; and that the discrepancies become smaller and smaller as the elastic force is lessened; so that, if means existed for comparing the different gases in states *equally distant* from their points of condensation, there is reason to believe that the law would be strictly fulfilled.

The experiments of Dalton and Gay-Lussac gave for the rate of expansion $\frac{1}{267}$ of the volume at 0°: this is no doubt too high. Those of Rudberg give $\frac{1}{274}$, those of Magnus and of Regnault $\frac{1}{273}$.

Conduction of Heat.

Different bodies possess very different conducting powers with respect to heat: if two similar rods, the one of iron, the other of glass, be held in the flame of a spirit-lamp, the iron will soon become too hot to be touched, while the glass may be grasped with impunity within an inch of the red-hot portion.

Experiments made by analogous but more accurate methods have established a numerical comparison of the conducting powers of many bodies. The following may be taken as a specimen:—

Silver,	1000
Copper,	736
Gold,	532
Brass,	236
Tin,	145
Iron,	119
Steel,	116
Lead,	85
Platinum,	84
German silver,	63
Bismuth,	18

As a class the metals are by very far the best conductors, although much difference exists between them; stones, dense woods, and charcoal follow next in order; then liquids in general, and lastly gases, whose conducting power is almost inappreciable.

Under favourable circumstances, nevertheless, both liquids and gases may become rapidly heated; heat applied to the bottom of the containing vessel is very speedily communicated to its contents; this, however, is not so much by conduction, as by convection, or carrying. A complete circulation is set up; the portions in contact with the bottom of the vessel get heated, become lighter, and rise to the surface, and in this way the heat becomes communicated to the whole. If these movements be prevented by dividing the vessel into a great number of compartments, the really low conducting power of the substance is made evident; and this is the reason why certain organic fabrics, as wool, silk, feathers, and porous bodies in general, the cavities of which are full of air, exhibit such feeble powers of conduction.

The circulation of heated water through pipes is now extensively applied to the warming of buildings and conservatories; and in chemical works a serpentine metal tube containing hot oil is often used for heating stills and evaporating pans; the two extremities of the tube are connected with the ends of another spiral built into a small furnace at a lower level, and an unintermitting circulation of the liquid takes place as long as heat is applied.

Specific Heat.

Equal weights of different substances having the same temperture require different amounts of heat to raise them to a given degree of temperature. If 1 lb. of water, at 100°, be mixed with 1 lb. at 40°, then, as is well known, a mean temperature of $\frac{100 + 40}{2} = 70°$ is obtained. In the same way the mean temperature is found when warm and cold oil, or warm and cold mercury, &c., are mixed together. But if 1 lb. of water at 100° be shaken with 1 lb. of olive-oil at 40°, or with 1 lb. of mercury at 40°, then, instead of the mean temperature of 70°, the temperature actually obtained will be 80° in the first case, 98° in the second; 20 degrees of heat, which the water (by cooling from 100° to 80°) gave to the same weight of oil, were sufficient to raise the oil 40°, that is, from 40° to 80°; and 2°, which the water lost by cooling from 100° to 98°, sufficed to heat an equal quantity of mercury 58°, namely, from 40° to 98°.

It is evident from these experiments that the quantities of heat which equal weights of water, olive-oil, and mercury, require to raise their temperature to the same height, are unequal, and that they are in the proportion of the numbers 1 : $\frac{20}{40}$: $\frac{2}{58}$, or 1 : $\frac{1}{2}$: $\frac{1}{29}$.

These quantities of heat, expressed relatively to the quantity of heat required to raise the temperature of an equal weight of water from 0° to 1° C., are called the specific heats of the various substances: thus the experiments just described show that the specific heat of olive oil is $\frac{1}{2}$, that is to say, the quantity of heat which would raise the temperature of any given quantity of olive oil from 0° to 1° would raise that of an equal weight of water only from 0° to $\frac{1}{2}$°, or of half that quantity of water from 0° to 1°.

The specific heats of bodies are sometimes said to measure their relative capacities for heat.

There are three distinct methods by which the specific heats of various substances may be estimated. The first of these is by observing the quantity of ice melted by a given weight of the substance heated to a particular temperature; the second is by noting the time which the heated body requires to cool down through a certain number of degrees; and the third is the method of mixture, on the principle illustrated; this latter method is preferred as the most accurate.

The determination of the specific heat of different substances has occupied the attention of many experimenters; among these Dulong and Petit, and recently Regnault and Kopp, deserve especial mention.

From the observations of these and other physicists, it follows that each body has its peculiar specific heat, and that the specific heat increases with increase of temperature. If, for example, the heat which the unit of water loses by cooling from 10° to 0° be marked at 10°, then the loss by cooling from 50° to 0° will be, not 50, corresponding to the difference of temperature, but 50·1. By cooling from 100° to 0° it is 100·5, and rises to 203·2 when the water is heated under great pressure to 200°, and afterwards cooled to 0°. Similar and even more striking differences have been found with other substances. It has also been proved that the specific heat of any substance is greater in the liquid than in the solid state. For example, the specific heat of ice is 0·504, that is, not more than half as great as that of liquid water.

It is remarkable that the specific heat of water is greater than that of all other solid and liquid substances, and is exceeded only by that of hydrogen. The specific heat of the solid parts of the crust of the globe is on an average $\frac{1}{4}$, and that of the atmosphere nearly $\frac{1}{4}$ that of water.

If the specific heat of any body within certain degrees of temperature be accurately known, then from the quantity of heat which this body gives out when quickly dipped into cold water, the temperature to which the body was heated may be determined. Pouillet has founded on this fact a method of measuring high temperatures, and for this purpose, with the help of the air-thermometer, he has determined the specific heat of platinum up to 1600°.

The determination of the specific heat of gases is attended with peculiar difficulties, on account of the comparatively large volume of small weights of gases. For many gases, however, satisfactory results have been obtained by the method of mixing.

When a gas expands, heat becomes latent, that is to say, insensible to the thermometer; in fact, the molecular motion which constitutes heat is converted into another kind of motion which overcomes the pressure to which the gas is subjected, and allows it to expand (see page 66). The amount of heat required, therefore, to raise a gas to any given temperature increases the more the gas in question is allowed to expand. The quantity of heat which the unit-weight of a gas requires in order to raise its temperature 1° without its volume undergoing any change (which can take place only by the pressure being simultaneously augmented) is called the specific heat of the gas *at constant volume.* The quantity of heat required by the unit-weight of a gas to raise its temperature 1°, it being at the same time allowed to dilate to such an extent that the pressure to which it is exposed remains unchanged, is called the specific heat of the gas *at constant pressure.* According to what has already been stated, the specific heat at constant pressure must be greater than that at constant volume. Dulong found, in the case of atmospheric air, of oxygen, of hydrogen, and of nitrogen, that the two specific heats are in the proportion 1·421 : 1. For carbon monoxide, however, he obtained the proportion of 1·423, for carbon dioxide 1·337, for nitrogen dioxide 1·343, and for olefiant gas 1·24 to 1. The exact determination of these ratios is extremely difficult, and the results of different physicists by no means agree.

The first satisfactory comparison of the specific heat of air with that of water was made by Count Rumford; later comparisons of the specific heat of various gases have been made by Delaroche and Bérard, Dulong and Regnault.

The first researches of Delaroche and Bérard furnished the results embodied in the following table :—

	Equal volumes.		Equal weights.	
	The volumes constant.	The pressure constant.	Air = 1.	Water = 1.
Atmospheric air,	1	1	1	0·2669
Oxygen,	1	1	0·9045	0·2414
Hydrogen,	1	1	14·4510	3·8569
Nitrogen,	1	1	1·0295	0·2748
Carbon monoxide,	1	1	1·0337	0·2759
Nitrogen monoxide,	1·227	1·160	0·7607	0·2030
Carbon dioxide,	1·249	1·175	0·7685	0·2051
Olefiant gas,	1·754	1·531	1·5829	0·4225

The latest and most trustworthy determinations are those of Regnault, given in the subjoined table, in the second column of which the specific heats of the several gases and vapours are compared with that of an equal weight of water taken as unity, and in the third, with that of an equal volume of air referred to its own weight of water as unity. The latter series of numbers is obtained by multiplying the numbers in the second column by the specific gravities of the respective gases and vapours referred to air as unity :—

Gases.	*Specific Gravity.* Air = 1.	*Specific Heat at Constant Pressure.*	
		For equal weights. Water = 1.	For equal volumes.
Atmospheric air,	1	0·2377	0·2377
Oxygen,	1·1056	0·2175	0·2405
Nitrogen,	0·9713	0·2438	0·2368
Hydrogen,	0·0692	3·4090	0·2359
Chlorine,	2·4502	0·1210	0·2965
Bromine vapour,	5·4772	0·0555	0·3040
Carbon monoxide,	0·9670	0·2450	0·2370
Carbon dioxide,	1·5210	0·2169	0·3307
Nitrogen monoxide,	1·5241	0·2262	0·3447
Nitrogen dioxide,	1·0384	0·2317	0·2406
Olefiant gas,	0·9672	0·4040	0·4106
Marsh gas,	0·5527	0·5929	0·3277
Aqueous vapour,	0·6220	0·4805	0·2989
Sulphuretted hydrogen,	1·1746	0·2432	0·2857
Sulphur dioxide,	2·2112	0·1544	0·3414
Vapour of carbon bisulphide,	2·6258	0·1569	0·4122
Hydrochloric acid,	1·2596	0·1852	0·2333
Ammonia,	0·5894	0·5084	0·2996

The researches of Delaroche and Bérard led them to suppose that the specific heat of gases increased rapidly as the temperature was raised, and that for a given volume of gas it increased in proportion to the density or tension of the gas. Regnault found, however, the quantity of heat which a given volume of gas requires to raise it to a certain temperature, to be independent of its density; and that for each degree between −30° and 225° it is constant. Carbon dioxide, however, forms an exception to this rule, its specific heat increasing with the temperature. In the table mean values for temperatures between 10° and 200° have been given.

Several physicists have held that the specific heats of elementary gases, referred to equal volumes, are identical. The numbers which Regnault found for chlorine and bromine, however, show that the law does not hold good for all elementary gases.

It has been already stated that, when a gas expands heat becomes latent. If a gas on expanding be not supplied with the requisite heat, its temperature falls on account of its own free heat becoming latent, that is to say, expended in overcoming pressure. On the other hand, if a gas be compressed, this latent heat becomes free, and causes an elevation of temperature, which, under favourable circumstances, may be raised to ignition; syringes by which tinder is kindled are constructed on this principle.

Change of State.

1. *Fusion and Solidification.*

Solid bodies when heated are expanded; many are liquefied, *i.e.*, they melt or fuse. The melting of solids is frequently preceded by a gradual softening, more especially when the temperature approaches the point of fusion. This phenomenon is observed in the case of wax or iron. In the case of other solids—of zinc and lead, for instance—and several other metals, this softening is not observed. Generally, bodies expand during the process of fusion; an exception to this rule is water, which expands during freezing (10 vol. of water produce nearly 11 vol. of ice), while ice when melting produces a proportionately smaller volume of water. The expansion of bodies during fusion, and at temperatures preceding fusion, or the contraction during solidification and further refrigeration, is very unequal. Wax expands considerably before fusing, and comparatively little during fusion itself. Wax, when poured into moulds, fills them perfectly during solidification, but afterwards contracts considerably. Stearic acid, on the contrary, expands very little before fusion, but rather considerably during fusion, and consequently pure stearic acid when poured into moulds solidifies to a rough porous mass, contracting little by further cooling. The addition of a little wax to stearic acid prevents the powerful contraction in the moment of solidification, and renders it more fit for being moulded.

Latent Heat of Fusion.—During fusion bodies absorb a certain quantity of heat, which is not indicated by the thermometer; at a given temperature—the melting point, for instance—a certain weight of substance contains when solid less heat than when liquid.

If equal weights of water at 0° and water at 79° be mixed, the temperature of the mixture will be the mean of the two temperatures, or 39·5°. If the same experiment be repeated with snow or finely-powdered ice at 0°, and water at 79°, the temperature of the whole will be only 0°, *but the ice will have been melted.*

$$\left.\begin{array}{l}\text{1 lb. of water at } 0^\circ\\ \text{1 lb. of water at } 79^\circ\end{array}\right\} = \text{2 lb. water at } 39{\cdot}5^\circ$$

$$\left.\begin{array}{l}\text{1 lb. of ice at } 0^\circ\\ \text{1 lb. of water at } 79^\circ\end{array}\right\} = \text{2 lb. water at } 0^\circ$$

In the last experiment, therefore, as much heat has been apparently lost as would have raised a quantity of water equal to that of the ice through a range of 79°.

The heat, thus become insensible to the thermometer in effecting the liquefaction of the ice, is called latent heat, or better, heat of fluidity.

Again, let a perfectly uniform source of heat be imagined, of such intensity that a lb. of water placed over it would have its temperature raised 5° per minute. Starting with water at 0°, in rather less than 16 minutes its temperature would have risen 79°; but the same quantity of ice at 0°, exposed for the same interval of time, would not have its temperature raised a single degree. But, then, it would have become water; the heat received would have been exclusively employed in effecting the change of state.

This heat is not lost, for when the water freezes it is again evolved. If a tall jar of water, covered to exclude dust, be placed in a situation where it shall be quite undisturbed, and at the same time exposed to great cold, the temperature of the water may be reduced 10° or more below its freezing point without the formation of ice; * but then, if a little agitation be communicated to the jar, or a grain of sand dropped into the water, a portion instantly solidifies, and the temperature of the whole rises to 0°; the heat disengaged by the freezing of a small portion of the water is sufficient to raise the whole contents of the jar 5°.

This curious condition of instable equilibrium shown by the very cold water in the preceding experiment, may be reproduced with a variety of solutions which tend to crystallise or solidify, but in which that change is for a while suspended. Thus, a solution of crystallised sodium sulphate in its own weight of warm water, left to cool in an open vessel, deposits a large quantity of the salt in crystals. If the warm solution, however, be filtered into a clean flask, which when full is securely corked and set aside to cool undisturbed, no crystals will be deposited, even after many days, until the cork is withdrawn and the contents of the flask are violently shaken. Crystallisation then rapidly takes place in a very beautiful manner, and the whole becomes perceptibly warm. The law above illustrated in the case of water is perfectly general. Whenever a solid becomes a liquid, a certain fixed and definite amount of heat disappears, or becomes latent; and conversely, whenever a liquid becomes solid, heat to a corresponding extent is given out.

The following table exhibits the melting points of several sub-

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* Fused bodies, when cooled down to or below their fusing point, frequently remain liquid, more especially when not in contact with solid bodies. Thus, water in a mixture of oil of almonds and chloroform, of specific gravity equal to its own, remains liquid to -10°; in a similar manner fused sulphur or phosphorus, floating in a solution of zinc chloride of appropriate concentration, retains the liquid condition at temperatures 40° below its fusing point. Liquid bodies, thus cooled below their fusing point, frequently solidify when touched with a solid substance, invariably when brought in contact with a fragment of the same body in the solid state. A body thus retained in the liquid state above its ordinary solidifying point, is said to be in a state of *surfusion* or *superfusion*.

stances, and their latent heats of fusion expressed in gram-degrees—that is to say, the numbers in the column headed "latent heat" denote the number of grams of water, the temperature of which would be raised 1° centigrade by the quantity of heat required to fuse one gram of the several solids:—

Substance.	Melting Point.	Latent Heat.	Substance.	Melting Point.	Latent Heat.
Mercury, . .	−39°	2·82	Tin, ...	235°	14·25
Phosphorus, .	+44	5·0	Silver, ...	1000	21·1
Lead, . . .	332	5·4	Zinc, ...	433	28·1
Sulphur, . .	115	9·4	Calcium chloride ($CaCl_2$, $6H_2O$),	28·5	40·7
Iodine, . . .	107	11·7	Potassium nitrate,	339	47·4
Bismuth, . .	270	12·6	Sodium nitrate, .	310·5	63·0
Cadmium, . .	320	13·6			

Freezing Mixtures.—When a solid substance can be made to liquefy by a weak chemical attraction, cold results, from sensible heat becoming latent. This is the principle of frigorific mixtures. When snow or powdered ice is mixed with common salt, and a thermometer plunged into the mass, the mercury sinks to 0° F. (−17·7° C.), while the whole after a short time becomes fluid by the attraction between the water and the salt; such a mixture is very often used in chemical experiments to cool receivers and condense the vapours of volatile liquids. Powdered crystallised calcium chloride and snow produce cold enough to freeze mercury. Even powdered potassium nitrate, or sal-ammoniac, or ammonium nitrate, dissolved in water, occasions a very notable depression of temperature; in every case, in short, in which solution is unaccompanied by energetic chemical action, cold is produced.

No relation can be traced between the actual melting point of a substance and its latent heat when in the fused state.

2. *Vaporisation and Condensation.*

A law of exactly the same kind as that above described affects universally the gaseous condition; change of state from solid or liquid to gas is accompanied by absorption of sensible heat, and the reverse by its disengagement. The latent heat of steam and other vapours may be ascertained by a mode of investigation similar to that employed in the case of water.

When water at 0° is mixed with an equal weight of water at 100°, the whole is found to possess the mean of the two temperatures, or 50°; on the other hand, 1 part by weight of *steam* at 100°, when condensed in cold water, is found to be capable of raising 5·4 parts of the latter from the freezing to the boiling point, or through a range of 100°. Now 100 × 5·4 = 540°; that is to say, steam at 100^{c}, in becoming water at 100°, parts with enough heat to raise a weight of water equal to its own (if it were possible) 540° of the thermometer, or 540 times its own weight of water one degree. When water passes into steam the same quantity of sensible heat becomes latent.

The vapours of other liquids seem to have less latent heat than that of water. The following table is by Dr Andrews of Belfast, and serves well to illustrate this point. The latent heats are expressed, as in the last table, in gram-degrees :—

	Latent Heat.
Vapour of water,	535·90°
,, alcohol,	202·40
,, ether,	90·45
,, oxalic ether,	72·72
,, acetic ether,	92·68
,, ethylic iodide,	46·87
,, wood spirit,	263·70
,, carbon bisulphide,	86·67
,, tin tetrachloride,	30·35
,, bromine,	45·66
,, oil of turpentine,	74·03

Boiling or Ebullition is occasioned by the formation of bubbles of vapour within the body of the evaporating liquid, which rise to the surface like bubbles of permanent gas. This occurs in different liquids at very different temperatures. Under the same circumstances, the boiling point is quite constant, and often becomes a physical character of great importance in distinguishing liquids which much resemble each other. A few cases may be cited in illustration :—

Substance.	Boiling Point.
Aldehyde,	20·8°
Ether,	34·9
Carbon bisulphide,	46·1
Alcohol,	78·4
Water,	100
Nitric acid, strong,	120
Oil of turpentine,	157
Sulphuric acid,	326·6
Mercury,	350

For ebullition to take place, it is necessary that the elasticity of the vapour should be able to overcome the cohesion of the liquid and the pressure upon its surface : hence the extent to which the boiling point may be modified.

Water, under the usual pressure of the atmosphere, boils at 100° (212° F.) ; in a partially exhausted receiver or on a mountain-top it boils at a much lower temperature ; and in the best vacuum of an air-pump, over oil of vitriol, which absorbs the vapour, it will often enter into violent ebullition while ice is in the act of forming upon the surface.

On the other hand, water confined in a very strong metallic vessel may be restrained from boiling by the pressure of its own vapour to an almost unlimited extent; a temperature of 177° or 204° is very easily obtained, and, in fact, it is said that water may be made red-hot, and yet retain its liquidity.

There is a very simple and beautiful experiment illustrative of the effect of diminished pressure in lowering the boiling point of a liquid. A little water is made to boil for a few minutes in a flask or retort placed over a lamp, until the air has been chased out, and the steam issues freely from the neck. A tightly fitting cork is then inserted, and the lamp at the same moment withdrawn. When the boiling ceases, it may be renewed at pleasure for a considerable time by pouring cold water on the flask, so as to condense the vapour within, and occasion a partial vacuum.

The nature of the vessel, or, rather, the state of its surface, exercises an influence upon the boiling point, and this to a much greater extent than was formerly supposed. It has long been noticed that in a metallic vessel water boils, under the same circumstances of pressure, at a temperature one or two degrees below that at which ebullition takes place in glass; but by particular management a much greater difference can be observed. If two similar glass flasks be taken, the one coated in the inside with a film of shellac, and the other completely cleansed by hot sulphuric acid, water heated over a lamp in the first will boil at 99·4°, while in the second it will often rise to 105° or even higher; a momentary burst of vapour then ensues, and the thermometer sinks a few degrees, after which it rises again. In this state, the introduction of a few metallic filings, or angular fragments of any kind, occasions a lively disengagement of vapour, while the temperature sinks to 100°, and there remains stationary. These remarkable effects must be attributed to an attraction between the surface of the vessel and the liquid.

When out of contact with solid bodies, liquids not only solidify with reluctance, but also assume the gaseous condition with greater difficulty. Drops of water or of aqueous saline solutions floating on the contact-surface of two liquids, of which one is heavier and the other lighter, may be heated from 10 to 20 degrees above the ordinary boiling point; explosive ebullition, however, is instantaneously induced by contact with a solid substance.

A cubic inch of water in becoming steam under the ordinary pressure of the atmosphere expands into 1696 cubic inches, or nearly a cubic foot.

Steam, *not in contact with water*, is affected by heat in the same manner as the permanent gases; its rate of expansion and increase of elastic force are practically the same. When water is present, the rise of temperature increases the quantity and density of the steam, and hence the elastic force increases in a far more rapid proportion.

This elastic force of steam in contact with water, at different temperatures, has been very carefully determined by Arago and Dulong, and lately by Magnus and Regnault. The force is expressed in atmospheres; the absolute pressure upon any given surface can be easily calculated, allowing 14·6 lb. per square inch to each atmosphere. The experiments were carried to twenty-five atmospheres—at which point the difficulties and danger became so great as to put a stop to the inquiry; the rest of the table is the result of calculations founded on the data so obtained :—

Pressure of Steam in Atmospheres.	Corresponding Temperature.	Pressure of Steam in Atmospheres.	Corresponding Temperature.
1	100°	13	194°
1·5	112	14	197
2	122	15	200·5
2·5	102	16	203
3	135	17	207
3·5	140·5	18	209
4	145·5	19	212
4·5	149	20	214
5	153	21	217
5·5	157	22	219
6	160	23	222
6·5	163	24	224
7	167	25	226
7·5	169	30	236
8	172	35	245
9	177	40	253
10	182	45	255
11	186	50	266
12	190		

It is very interesting to know the amount of heat requisite to convert water of any given temperature into steam of the same or another given temperature. The most exact experiments on this subject have been made by Regnault. He arrived at this result, that when the unit-weight of steam at the temperature t° is converted into water of the same temperature, and then cooled to 0°, its gives out the quantity of heat T, which is represented by the formula :—

$$T = 606{\cdot}5 + 0{\cdot}305\, t.$$

This formula appears to hold good for temperatures both above and below the ordinary boiling point of water. The following table gives the values of T, corresponding to the respective temperatures in the first column :—

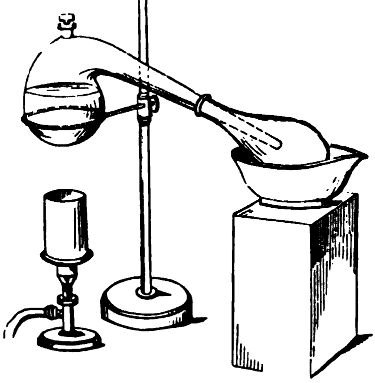
t	T
0°	606·5°
50	621·7
100	637·0
150	652·2
200	667·5

T is called the total heat of steam, being the heat required to raise water from 0° to t, together with that which becomes latent by the transformation of water at $t°$ into steam at $t°$. Regnault states, as a result of some very delicate experiments, that the heat necessary to raise a unit-weight of water from 0° to $t°$ is not exactly denoted by t; the discrepancy, however, is so small that it may be disregarded. Employing the approximate value, the latent heat of steam, L, at any temperature will be found by subtracting t from the total heat; or, according to the formula:—

$$L = 606{\cdot}5 - 0{\cdot}695\,t.$$

This equation shows us the remarkable fact that the latent heat of steam diminishes as the temperature rises. Before Regnault's experiments were made, two laws of great simplicity were generally admitted, one of which, however, contradicted the other. Watt concluded, from experiments of his own, as well as from theoretical speculations, that the total heat of steam would be the same at all temperatures. Were this true, equal weights of steam passed into cold water would always exhibit the same heating power, no matter what the temperature of the steam might be. Exactly the same *absolute* amount of heat, and consequently the same quantity of fuel, would be required to evaporate a given weight of water *in vacuo* at a temperature which the hand can bear, or under great pressure and at a high temperature. Watt's law, though agreeing well with the rough practical results obtained by engineers, is only approximately true; and the same may be said of the deductions which have just been made from it. The second law, in opposition to Watt's, is that of Southern, stating the latent heat of steam to be the same at all temperatures. Regnault's researches have shown that neither Watt's law (T constant) nor Southern's law (L constant) is correct.

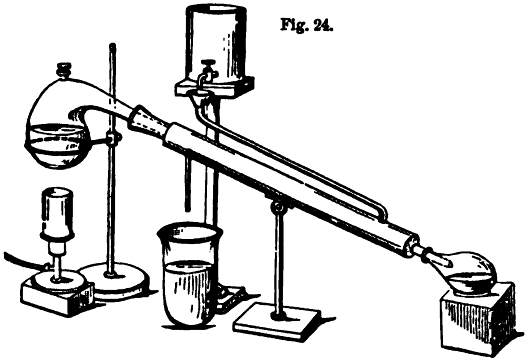
Fig 23.



Distillation.—The process of distillation is very simple: its object is either to separate substances which rise in vapour at different temperatures, or to part a volatile liquid from a substance incapable of volatilisation. The same process applied to bodies which pass directly from the solid to the gaseous condition, and the reverse, is called *sublimation*. Every distillatory apparatus consists essentially of a boiler, in which the vapour is raised, and of a condenser, in which it returns to the liquid or solid condition. In the still employed for manufacturing purposes, the latter is usually a spiral metal tube immersed in a tub of water. The common retort and receiver constitute the simplest arrangement for distillation on the small scale; the retort is heated by a gas lamp, and the receiver is kept cool, if necessary, by a wet cloth, or it may be surrounded with ice (fig. 23).

Liebig's condenser (fig. 24) is a very valuable instrument in the laboratory; it consists of a glass tube tapering from end to end, fixed by perforated corks in the centre of a metal pipe, provided with tubes so arranged that a current of cold water may circulate through the apparatus. By putting ice into the little cistern, the water may be kept at 0°, and extremely volatile liquids condensed.

Fig. 24.

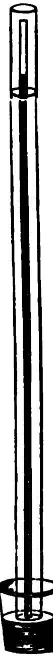


Tension of Vapours.—Liquids evaporate at temperatures below their boiling points; in this case the evaporation takes place slowly from the surface. Water, or alcohol, exposed in an open vessel at the temperature of the air, gradually disappears; the more rapidly, the warmer and drier the air.

This fact was formerly explained by supposing that air and gases in general had the power of dissolving and holding in solution certain quantities of liquids, and that this power increased with the temperature; such an idea is incorrect.

If a barometer-tube be carefully filled with mercury and inverted in the usual manner, and then a few drops of water passed up the tube into the vacuum above, a very remarkable effect will be observed,—the mercury will be depressed to a small extent, and this depression will increase with increase of temperature. Now, as the space above the mercury is void of air, and the weight of the few drops of water quite inadequate to account for this depression, it must of necessity be imputed to the vapour which instantaneously rises from the water into the vacuum; and that this effect is really due to the elasticity of the aqueous vapour, is easily proved by exposing the barometer to a heat of 100°, when the depression of the mercury will be complete, and it will stand at the same level within and without the tube; indicating that at that temperature the elasticity of the vapour is equal to that of the atmosphere—a fact which the phenomenon of ebullition has already shown.

Fig. 25.



By placing over the barometer a wide open tube dipping into the mercury below (fig. 25), and then filling this tube with water at different temperatures, the tension of the aqueous vapour for each degree of the thermometer may be accurately determined by its depressing effect upon the mercurial column; the same power which forces the latter *down* one inch against the pressure of the atmosphere, would of course *elevate* a column of mercury to the same height against a vacuum, and in this way the tension may be conveniently expressed. The following table was drawn up by Dalton, to whom we owe the method of investigation:—

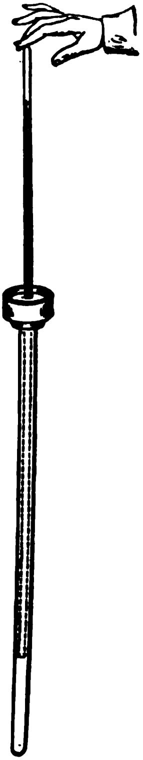
Temperature. F.	Temperature. C.	Tension in Inches of Mercury.	Temperature. F.	Temperature. C.	Tension in Inches of Mercury.
32°	0°	0.200	130°	54·4°	4·34
40	4·4	0·263	140	60	5·74
50	10	0·375	150	65·5	7·42
60	15·5	0·524	160	71·1	9·46
70	21·1	0·721	170	76·6	12·13
80	26·6	1·000	180	82·2	15·15
90	32·2	1·360	190	87·7	19·00
100	37·7	1·860	200	93·3	23·64
110	43·3	2·530	212	100	30·00
120	48·8	3·330			

Another table representing the tension of the vapour of water, drawn up by Regnault, is given in the Appendix to this volume.

Other liquids tried in this manner are found to emit vapours of greater or less tension, for the same temperature, according to their different degrees of volatility; thus, a little ether introduced into the tube depresses the mercury 10 inches or more at the ordinary temperature of the air; oil of vitriol, on the other hand, does not emit any sensible quantity of vapour until a much greater heat is applied; and that given off by mercury itself in warm summer weather, although it may be detected by very delicate means, is far too little to exercise any effect upon the barometer. In the case of water, the evaporation is quite distinct and perceptible at the lowest temperatures when frozen to solid ice in the barometer-tube; snow on the ground, or on a housetop, may often be noticed to vanish, from the same cause, day by day in the depth of winter, when melting is impossible.

There exists for each vapour a state of density which it cannot pass without losing its gaseous condition, and becoming liquid; this is called the *condition of maximum density.* When a volatile liquid is introduced in sufficient quantity into a vacuum, this condition is always reached, and then evaporation ceases. Any attempt to increase the density of this vapour by compressing it into a smaller space will be attended by the liquefaction of a portion, the density of the remainder being unchanged. If a little ether be introduced into a barometer, and the latter slowly sunk into a very deep cistern of mercury (fig. 26) it will be found that the height of the column of mercury in the tube above that in the cistern remains unaltered until the upper extremity of the barometer approaches the surface of the metal in the column, and all the ether has become liquid. It will be observed also, that, as the tube sinks, the stratum of liquid ether increases in thickness, but no increase of elastic force occurs in the vapour above it, and consequently, no increase of density: for tension and density are always, under ordinary circumstances at least, directly proportionate to each other.

Fig. 26.



The maximum density of vapours is dependent upon the temperature; it increases rapidly as the temperature rises. This is well shown in the case of water. Thus, taking the spec. grav. of atmospheric air at 100° = 1000, that of aqueous vapour in its greatest state of compression for the temperature will be as follows:—

Temperature. F.	Temperature. C.	Specific Gravity.	Weight of 100 Cubic Inches.
32°	0°	5·690	0·136 grains.
50	10	10·293	0·247 ,,
60	15·5	14·108	0·338 ,,
100	37·7	46·500	1·113 ,,
150	65·5	170·293	4·076 ,,
212	100	625·000	14·962 ,,

The last number was experimentally found by Gay-Lussac; the others are calculated from that by the aid of Dalton's table of tensions, on the assumption that steam, not in a state of saturation, that is, below the point of greatest density, obeys Boyle's law (which is, however, only approximately true), and that when it is cooled it contracts like the permanent gases.

Thus, there are two distinct methods by which a vapour may be reduced to the liquid form—*pressure*, by causing increase of density until the point of maximum density for a given temperature is reached; and *cold*, by which the point of maximum density is itself lowered. The most powerful effects are produced when both are conjoined.

For example, if 100 cubic inches of vapour of water at 100° F., in the state above described, had its temperature reduced to 50° F., not less than 0·89[*] grain of liquid water would necessarily separate, or very nearly eight-tenths of the whole.

Evaporation into a space filled with air or gas follows the same law as evaporation into a vacuum; as much vapour rises, and the condition of maximum density is assumed in the same manner, as if the space were perfectly empty; the sole difference lies in the length of time required. When a liquid evaporates into a vacuum, the point of greatest density is attained at once, while in the other case some time elapses before this happens: the particles of air appear to oppose a sort of mechanical resistance to the rise of the vapour. The ultimate effect is, however, precisely the same.

When to a quantity of perfectly dry gas confined in a vessel closed by mercury, a little water is added, the latter immediately begins to evaporate, and after some time as much vapour will be found to have risen from it as if no gas had been present, the quantity depending entirely on the temperature to which the whole is subjected. The tension of this vapour will add itself to that of the gas, and produce an expansion of volume, which will be indicated by an alteration of level in the mercury.

Vapour of water exists in the atmosphere at all times, and in all situations, and there plays a most important part in the economy of nature. The proportion of aqueous vapour present in the air is subject to great variation, and it often becomes important to determine its quantity. This is easily done by the aid of the foregoing principles.

Dew-point.—If the aqueous vapour be in its condition of greatest possible density for the temperature, or, as it is frequently but most incorrectly, expressed, the air be saturated with vapour of water, the slightest reduction of temperature will cause the deposition of a portion in the liquid form. If, on the contrary, as is almost always in reality the case, the vapour of water be *below* its state of maximum density, that is, in an expanded condition, it is clear that a considerable fall of temperature may occur before liquefaction commences. The degree at which this takes place is called the dew-point, and it is determined with great facility by a very simple method. A little cup of thin tin-plate or silver, well polished, is filled with water at the temperature of the air, and a delicate thermometer inserted. The water is then cooled by dropping in fragments of ice, or dissolving in it powdered sal-ammoniac, until moisture begins to make its appearance on the outside, dimming the bright metallic surface. The temperature of the dew-point is then read off upon the thermometer, and compared with that of the air.

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[*] 100 cub. inch. aqueous vapour at 100° F., weighing 1·113 grain, would at 50° F. become reduced to 91·07 cub. inch., weighing 0·225 grain.

Suppose, by way of example, that the latter were 70° F., and the dew-point 50° F., the elasticity of the watery vapour present would correspond to a maximum density proper to 50° F., and would support a column of mercury 0·375 inch high. If the barometer on the spot stood at 30 inches, therefore, 29·625 inches would be supported by the pressure of the dry air, and the remaining 0·375 inch by the vapour. Now, a cubic foot of such a mixture must be looked upon as made up of a cubic foot of dry air, and a cubic foot of watery vapour, occupying the same space, and having tensions indicated by the numbers just mentioned. A cubic foot, or 1728 cubic inches of vapour at 70° F., would become reduced by contraction, according to the usual law, to 1662·8 cubic inches at 50° F.; this vapour would be at its maximum density, having the specific gravity pointed out in the table: hence 1662·8 cubic inches would weigh 4·11 grains. The weight of the aqueous vapour contained in a cubic foot of air will thus be ascertained. In this country the difference between the temperature of the air and the dew-point seldom reaches 30° F. (16·6° C.); but in the Deccan, with a temperature of 90° F. (32·2° C.), the dew-point sinks as low as 29° F., making the degrees of dryness 61° F.[*]

Liquefaction of Gases.—The perfect resemblance in every respect which vapours bear to permanent gases, led, very naturally, to the idea that the latter might, by the application of suitable means, be made to assume the liquid state, and this surmise has been verified to a great extent by the experiments of Faraday. Out of the small number of such substances tried, no fewer than eight gave way; and it is quite fair to infer that, had means of sufficient power been at hand, the rest would have shared the same fate, and proved to be nothing more than the vapours of volatile liquids in a state very far removed from that of their maximum density. The subjoined table represents the results of Faraday's first investigations, with the pressure in atmospheres, and the temperatures at which the condensation takes place.

	Atmospheres.	Temperatures.	
		F.	C.
Sulphur dioxide,	2	45°	7·2°
Hydrogen sulphide,	17	50	10
Carbon dioxide,	36	32	0
Chlorine,	4	60	15·5
Nitrogen monoxide,	50	45	7·2
Cyanogen,	3·6	45	7·2
Ammonia,	6·5	50	10
Hydrochloric acid,	40	50	10

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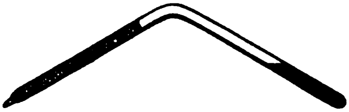
[*] Daniell, Introduction to Chemical Philosophy, p. 154.

The method of proceeding was very simple: the materials were sealed up in a strong narrow tube, together with a little pressure-gauge, consisting of a slender tube closed at one end, and having within it, near the open extremity, a globule of mercury. The gas being disengaged by heat, accumulated in the tube, and by its own pressure brought about condensation. The force required for this purpose was judged of by the diminution of volume of the air in the gauge.

Fig. 27.



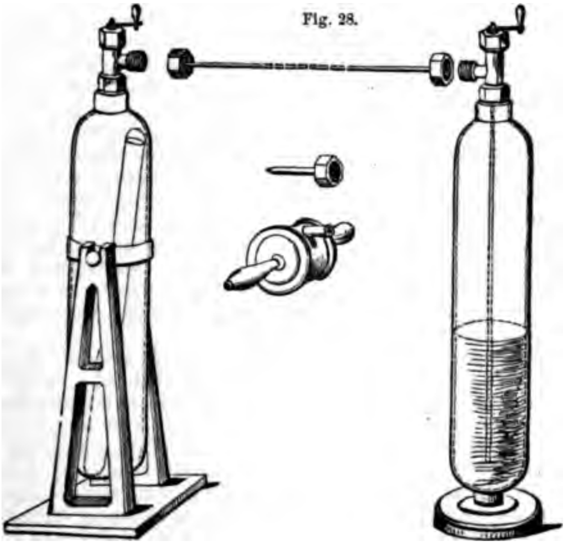
By the use of narrow green glass tubes of great strength, powerful condensing syringes, and an extremely low temperature, produced by means to be presently described, olefiant gas, hydriodic and hydrobromic acids, phosphoretted hydrogen, and the gaseous fluorides of silicon and boron, were successively liquefied. Oxygen, hydrogen, nitrogen, nitrogen dioxide, carbon monoxide, and marsh gas, refused to liquefy even at − 166° F. while subjected to pressures varying from 27 to 58 atmospheres.

Sir Isambard Brunel, and, more recently, M. Thilorier, of Paris, succeeded in obtaining liquid carbon dioxide (commonly called carbonic acid) in great abundance. Thilorier's apparatus (fig 28) consists of a pair of extremely strong metallic vessels, one of which is destined to serve the purpose of a retort, and the other that of a receiver. They are made either of thick cast iron or gun metal, or, still better, of the best and heaviest boiler-plate, and are furnished with stop-cocks of a peculiar kind, the workmanship of which must be excellent. The generating vessel or retort has a pair of trunnions upon which it swings in an iron frame. The joints are secured by collars of lead, and every precaution is taken to prevent leakage under the enormous pressure the vessel has to bear. The receiver resembles the retort in every respect; it has a similar stop-cock, and is connected with the retort by a strong copper tube and a pair of union screw-joints; a tube passes from the stop-cock downwards, and terminates near the bottom of the vessel.

The operation is thus conducted: 2¾ lb. of acid sodium carbonate, and 6¼ lb. of water at 100° F., are introduced into the generator; oil of vitriol to the amount of 1½ lb. is poured into a copper cylindrical vessel, which is lowered down into the mixture, and set upright; the stop-cock is then screwed into its place, and forced home by a spanner and mallet. The machine is next tilted up on its trunnions, that the acid may run out of the cylinder and mix with the other contents of the generator; and this mixture is favoured by swinging the whole backwards and forwards for a few minutes, after which it may be suffered to remain a little time at rest.

The receiver, surrounded with ice, is next connected with the generator, and both cocks are opened; the liquefied carbon dioxide distils over into the colder vessel, and there again in part condenses. The cocks are now closed, the vessel is disconnected, the cock of the generator opened to allow the contained gas to escape; and, lastly, when the issue of gas *has quite ceased*, the stop-cock itself is unscrewed, and the sodium sulphate turned out. This operation must be repeated five or six times before any considerable quantity of liquefied carbon dioxide will have accumulated in the receiver.

Fig. 28.



When the receiver thus charged has its stop-cock opened, a stream of the liquid is forcibly driven up the tube by the elasticity of the gas contained in the upper part of the vessel.

The experimenter incurs great personal danger in using this apparatus, unless the utmost care be taken in its management. A dreadful accident occurred in Paris by the bursting of one of the iron vessels.

Liquid carbon dioxide is also very frequently prepared by means of an apparatus constructed by Natterer, of Vienna, which enables the experimentalist to work with less risk. The gas, disengaged by means of sulphuric acid from acid potassium carbonate, is pumped by means of a force-pump into a wrought iron-vessel, exactly as the air is pumped into the receiver of an air-gun. When a certain pressure has been reached, the gas is liquefied, and if the pressure be continued considerable quantities of the liquid carbon dioxide may be thus obtained. By this apparatus, nitrous oxide has been condensed to a liquid without the use of frigorific mixtures.

Complete Vaporisation of Liquids under great Pressures.—When the temperature of a liquid is raised sufficiently high, vaporisation occurs under the highest pressure to which the substance can be subjected. Alcohol, ether, or rock-oil, enclosed in a tube of strong glass or iron, is completely converted into vapour, only when the space not occupied by the liquid is somewhat greater than the volume of the liquid itself. With rock-oil the empty space may be somewhat smaller than with alcohol, and with ether still less. Alcohol when thus heated acquires increased mobility, expands to twice its original volume, and is then suddenly converted into vapour. This change takes place at 207° C. (404·6° F.), when the alcohol occupies just half the volume of the tube; if the tube is more than half filled with alcohol, it bursts when heated. A glass tube one-third filled with water becomes opaque when heated, and bursts after a few seconds. If this chemical action of the water on the glass be diminished by the addition of a little carbonate of soda, the transparency of the glass will be much less impaired; and if the space occupied by the water be $\frac{1}{4}$ of the whole tube, the liquid will be converted into vapour at about the temperature of melting zinc. These observations were made by Cagniard de Latour in 1822.

In like manner Dr Andrews has observed that when liquid carbon dioxide is gradually heated in a sealed tube to 31°, the surface of demarcation between the liquid and gas becomes fainter, loses its curvature, and at last disappears. The space is then occupied by a homogeneous fluid, which exhibits, when the pressure is suddenly diminished, or the temperature slightly lowered, a peculiar appearance of moving or flickering striæ throughout its entire mass. At temperatures above 31° no apparent liquefaction of carbon dioxide or separation into two distinct forms of matter can be effected, even under a pressure of 300 or 400 atmospheres. Similar results are obtained with nitrous oxide.

It appears indeed that there exists for every liquid a temperature, called by Andrews the "critical point," above which no amount of pressure is sufficient to retain it in the liquid form; it is therefore not surprising that mere pressure, however intense, should fail to liquefy many bodies which usually exist in the form of gas.

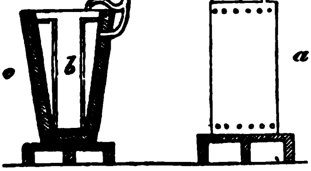
Under the enormous pressures to which gases can be thus subjected, without liquefaction, they are found to deviate greatly from the laws of Boyle and Gay-Lussac (pp. 25, 30). Andrews has recently found that carbon dioxide, at 60·7° under a pressure of 223 atmospheres, is reduced to $\frac{1}{477}$ of its original volume, or to less than one-half the volume it should occupy if it contracted according to Boyle's law. The co-efficient of expansion of the same gas by heat increases rapidly with the pressure; between 6° and 64° it is 1½ times as great under 22 atmospheres, and more than 2½ times as great at 40 atmospheres, as at the pressure of 1 atmosphere.*

Cold produced by Evaporation.—This effect has been already adverted to: it arises from the conversion of sensible heat into latent by the rising vapour, and may be illustrated in a variety of ways. Ether dropped on the hand produces the sensation of great cold; and water contained in a thin glass tube, surrounded by a bit of rag, is speedily frozen when the rag is kept wetted with ether.

Ice-making machines and refrigerators are constructed on this principle. Harrison's apparatus for freezing water consists of a multitubular boiler containing about 10 gallons of ether and immersed in a trough of salt water. The boiler is connected with an exhausting pump, by the working of which the ether is rapidly volatilised, thereby cooling the boiler and the salt water surrounding it to about 24° F. (−4·45° C.) This cold water is made to flow through a channel in which are placed a number of vessels containing the water to be frozen, and when its temperature has been thus raised to about 28°, it is pumped back again into the trough containing the boiler, and then again cooled by the evaporation of the ether. In this manner a constant supply of cold salt water is kept up. The ether which is evaporated is condensed in a worm surrounded by cold water, and returned with very little loss to the boiler.†

A simpler freezing apparatus is that of Carré, in which cold is produced by the rapid evaporation of liquefied ammonia gas. It consists essentially of a cylindrical boiler *a*, fig. 29, holding about two gallons, filled to about three-fourths of its capacity with a strong aqueous solution of ammonia, and connected by pipes with a wrought-iron annular condenser or freezer *c*. The boiler is first placed in a furnace, and the freezer in water cooled to 12° C. (53·6° F.) The boiler is heated to 130° C., whereupon ammonia gas is given off, and condenses in the freezer, together with about one-tenth of its own weight of water. This operation being completed, the boiler is removed from the fire and immersed in cold water; the freezer, wrapped in very dry flannel, is

Fig 29.



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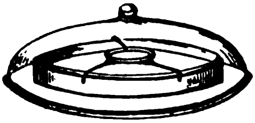
* Journal of the Chemical Society, 1876, vol. ii. p. 162.

† A figure of this apparatus is given in the Pharmaceutical Journal, vol. xvi. p. 477.

placed outside, and the vessel containing the water to be frozen is placed in the cylindrical space *b*. As the boiler cools, the ammonia gas with which it is filled is redissolved, and the pressure being thus diminished, the ammonia which has been liquefied in *c* is again volatilised, and passes over towards *a*, to redissolve in the water which has remained in the boiler. This rapid evaporation of the ammonia causes a great absorption of heat, whereby the vessel *c* is reduced to a very low temperature, and the water contained in it is frozen. To obtain better contact between the sides of the vessel *b* and the freezer, alcohol is poured between them. This apparatus gives about 4 ℔ of ice in an hour at a price of about a farthing a pound; but large continuously working apparatus have been constructed which produce as much as 800 ℔ of ice in an hour.*

Water may also be frozen by the cold resulting from its own evaporation. When a little water is put into a watch-glass, supported by a triangle of wire over a shallow glass dish of sulphuric acid placed on the plate of a good air-pump, the whole covered with a low receiver, and the air withdrawn as perfectly as possible, the water is in a few minutes converted into a solid mass of ice. The absence of the air, and the rapid absorption of watery vapour by the oil of vitriol, induce such quick evaporation that the water has its temperature almost immediately reduced to the freezing point.

Fig. 30.



The same apparatus is constantly used in the laboratory for drying substances which cannot bear heating without decomposition. Frequently also the air-pump is dispensed with, and the substance to be dried is simply placed over a vessel containing strong sulphuric acid, quicklime, or some other substance which absorbs moisture very rapidly, and covered over with a bell jar. Such an apparatus, with or without the air-pump, is called an *Exsiccator*.

All means of producing artificial cold yield, however, in intensity to that derived from the evaporation of the liquefied carbon dioxide just mentioned. When a jet of that liquid is allowed to issue into the air from a narrow aperture, so intense a degree of cold is produced by the vaporisation of a part, that the remainder freezes to a solid, and falls in a shower of snow. By suffering this jet of liquid to flow into the metal box shown in fig. 28, a large quantity of the solid oxide may be obtained; it closely resembles snow in appearance, and when held in the hand occasions a painful sensation of cold, while it gradually disappears. When it is mixed with a little ether, and poured upon a mass of mercury, the latter is almost instantly frozen, and in this way pounds of the solidified metal may be obtained. The addition of the ether facilitates the contact of the carbon dioxide with the mercury.

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* See Richardson and Watts's Chemical Technology, part v. p. 296.

The temperature of a mixture of solid carbon dioxide and ether in the air, measured by a spirit-thermometer, was found to be −106° F.; when the same mixture was placed beneath the receiver of an air-pump, and exhaustion rapidly made, the temperature sank to −166° F. This was the method of obtaining extreme cold employed by Faraday in his last experiments on the liquefaction of gases. Under such circumstances, the liquefied hydriodic and hydrobromic acids, sulphur dioxide, carbon dioxide, nitrogen monoxide, hydrogen sulphide, cyanogen, and ammonia, froze to colourless transparent *solids*, and alcohol became thick and oily.

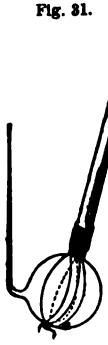
Determination of the Specific Gravity of Gases and Vapours.

To determine the specific gravity of a gas, a large glass globe is filled with the gas to be examined, in a perfectly pure and dry state, having a known temperature, and an elastic force equal to that of the atmosphere at the time of the experiment. The globe so filled is weighed. It is then exhausted at the air-pump as far as possible, and again weighed. Lastly, it is filled with dry air, the temperature and pressure of which are known, and its weight once more determined. On the supposition that the temperature and elasticity are the same in both cases, the specific gravity is at once obtained by dividing the weight of the gas by that of the air.

The globe or flask must be made very thin, and fitted with a brass cap, surmounted by a small but excellent stop-cock. A delicate thermometer should be placed in the inside of the globe, secured to the cap. The gas must be generated at the moment, and conducted at once into the previously exhausted vessel, through a long tube filled with fragments of pumice moistened with oil of vitriol, or some other extremely hygroscopic substance, by which it is freed from all moisture. As the gas is necessarily generated under some pressure, the elasticity of that contained in the filled globe will slightly exceed the pressure of the atmosphere; and this is an advantage, since, by opening the stop-cock for a single instant, when the globe has attained an equilibrium of temperature, the tension becomes exactly that of the air, so that all barometrical correction is avoided, unless the pressure of the atmosphere should sensibly vary during the time occupied by the experiment. It is hardly necessary to observe that the greatest care must also be taken to purify and dry the air used as the standard of comparison, and to bring both gas and air as nearly as possible to the same temperature, so as to obviate the necessity of a correction, or at least to reduce almost to nothing the errors involved by such a process.

VAPOURS.—1. *Dumas' Method.* This method consists in determining the weight of a given volume of the vapour at a known pressure and temperature. A large glass globe about three inches in diameter is taken, and its neck softened and drawn out in the blowpipe flame, as represented in fig. 31; this is accurately weighed. About 100 grains of the volatile liquid are then introduced, by gently warming the globe and dipping the point into the liquid, which is then forced upwards by the pressure of the air as the vessel cools. The globe is next firmly attached by wire to a handle, in such a manner that it may be plunged into a bath of boiling water or heated oil, and steadily held with the point projecting upwards. The bath must have a temperature considerably above that of the boiling point of the liquid. The latter becomes rapidly converted into vapour, which escapes by the narrow orifice, chasing before it the air of the globe. When the issue of vapour has wholly ceased, and the temperature of the bath appears nearly uniform, the open extremity of the point is hermetically sealed by a small blowpipe flame. The globe is removed from the bath, suffered to cool, cleansed if necessary, and weighed, after which the neck is broken off beneath the surface of water which has been boiled and cooled out of contact of air, or (better) under mercury. The liquid enters the globe, and, if the expulsion of the air by the vapour has been complete, fills it; if otherwise, an air-bubble is left, whose volume can be easily ascertained by pouring the liquid from the globe into a graduated jar, and then refilling the globe, and repeating the same observation. The capacity of the vessel is thus at the same time known; and these are all the data required.* An example will render the whole intelligible.

Fig. 31.



Determination of the Vapour-density of Acetone.

Capacity of globe, ...	31·61 cubic inches.
Weight of globe filled with dry air at 52° F. and 30·24 inches barometer, .	2070·88 grains.
Weight of globe filled with vapour at 212° F. temp. of the bath at the moment of sealing the point, and 30·24 inches barometer, ...	2076·81 grains.
Residual air, at 45° F. and 30·24 inches barometer, ...	0·60 cubic inches.

31·61 cubic inches of air at 52° and 30·24 in. bar. = 32·36 cub. inches at 60° F. and 30 inch bar., weighing . 10·035 grains.

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* Messrs Playfair and Wanklyn have described an important modification of this process, whereby the densities of a vapour at temperatures below the boiling point of the liquid may be determined. This object is attained by mixing the vapour of the body with a measured volume of a permanent gas—hydrogen, for instance.—*Journ. of the Chem. Soc.* vol. xv. p. 143.

Hence, weight of empty globe, 2070·88 − 10·035 = 2060·845 grains.

0·6 cubic inch of air at 45° = 0·8 cub. inch at 212°; weight of do. by calculation = 0·191 grain.

31·61 − 0·8 = 30·81 cubic inches of vapour at 212° and 30·24 in. bar., which, *on the supposition that it would bear cooling to 60° without liquefaction*, would, at that temperature, and under a pressure of 30 inch. bar., become reduced to 24·18 cubic inches.

Hence,

Weight of globe and vapour, . . .	2076·810	grains.
„ residual air, ...	0·191	
	2076·619	„
Weight of globe, ...	2060·845	„
Weight of the 24·18 cubic inches of vapour,	15·774	„
Consequently, 100 cubic inches of such vapour must weigh	65·23	„
100 cubic inches of air, under similar circumstances, weigh	31·01	„

$\frac{65 \cdot 23}{31 \cdot 01} = 2 \cdot 103$, the specific gravity of the vapour in question, that of being unity.

Or, the weight of 100 cubic inches of hydrogen being 2·147 grains, $\frac{65 \cdot 23}{2 \cdot 14} = 30 \cdot 38$ is the specific gravity of acetone vapour referred to hydrogen as unity.

The vapour-density (D) may also be readily calculated by means of the formula:

$$D = \frac{P + Vn_t}{(V - v)\, n'_t} .$$

P = difference of weight (in grams) between the globe filled with air and when filled with vapour.

V = capacity of globe in cubic centimeters.

n_t = weight of one cubic centimeter of air at the temperature at which the globe filled with air was weighed.

n'_t = weight of one cubic centimeter of air at the temperature of sealing the globe.

The values of n_t and n'_t (in grams) for each degree centigrade from 0 to 300° are given in the Appendix, Table VII.

In very exact experiments account must be taken of the change of capacity of the glass globe by the high temperature of the bath. When this correction is neglected, the density of the vapour will come out a little too high. The error of the mercurial thermometer at high temperatures is, however, in the opposite direction.

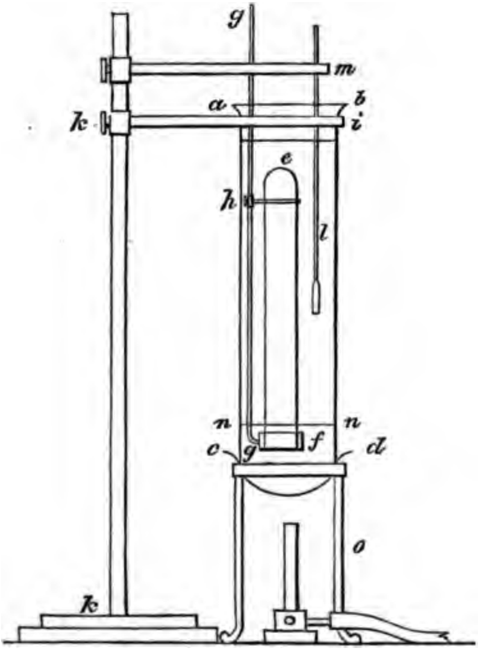
The preceding method is applicable to the determination of the vapour-densities of all substances whose boiling points are within the range of the mercurial thermometer, that is to say, not exceeding 300° C., and therefore to nearly all volatile organic compounds; indeed, there are but few such compounds which can bear higher temperatures without decomposition. But for mineral substances, such as sulphur, iodine, volatile metallic chlorides, &c., it is often necessary to employ much higher temperatures; and for such cases a modification of the process has been devised by Deville and Troost. It consists in using a globe of porcelain instead of glass, heating it in the vapour of a substance whose boiling point is known and constant, and sealing the globe by the flame of the oxy-hydrogen blowpipe. The vapours employed for this purpose are those of mercury, which boils at 350° C.; of sulphur, which boils at 440°; of cadmium, boiling at 860°; and of zinc, boiling at 1040°. The use of these liquids of constant boiling point obviates the necessity of determining the temperature in each experiment, which at such degrees of heat would be very difficult.

2. *Gay-Lussac's Method.*—This method consists in ascertaining the volume occupied by a given weight of a substance when converted into vapour at a known temperature and pressure. For this purpose a small bulb of very thin glass with a capillary neck is weighed, filled with the liquid, sealed and again weighed, the difference of the two weighings of course giving the weight of the liquid. It is then introduced into a graduated glass jar filled with mercury, inverted in a basin of mercury, and immersed in a bath of water or oil, and heat is applied to the bath till the bulb bursts, and the liquid is converted into vapour, which depresses the mercury in the gas-jar to a certain level. This is read off, together with the temperature of the bath and the height of the barometer, and from these readings the volume of the vapour at a certain pressure and temperature. A convenient apparatus for the purpose is represented in figure 32. It consists of a cylinder of rather thin glass, $a\ b\ c\ d$ in shape like a very large test-tube, about 16 or 18 inches long, and 5 or 6 in diameter. At the lower and closed end it is rounded, and care must be taken that it is thin enough to stand the application of heat, and yet strong enough to bear the weight of the mercury and the rest of the apparatus which will have to be inserted. A small and rather light gas-jar e, divided into inches or half cubic centimeters, is supported at its lower end by an iron cup f, attached to a rod $g\ g$ of the same metal. In the engraving it is represented in the act of being lowered into its place. The upper end of the jar is kept steady by the ring h, which slides on the rod $g\ g$. The cylinder is retained in its vertical position by the ring i sliding on the massive retort-stand $k\ k$. The rod $g\ g$ and the thermometer l are supported by the arm m, also attached to the retort-stand. The cylinder being charged up to the line $n\ n$ with mercury, the gas-jar l, filled with mercury, and having the glass bulb containing the liquid to be examined inserted, is placed in the position seen in the figure. The cylinder

is then to be filled with water, or neat's-foot oil, until the gas-jar is covered for at least an inch. The cylinder may be supported on wire-gauze over the tripod *o*, or in any other convenient manner. Heat may be applied by means of a Bunsen's burner.

Great care must be taken, in passing the bulb up into the gas-jar, to prevent fracture. The most convenient way of accomplishing this, is to place the lower end of the jar in a mercurial trough, and to incline it to an angle of about 45°. The bulb is then to be held between the thumb and first two fingers, the tail towards the palm of the hand; it is then to be presented to the opening of the gas-jar, and when inserted is to be let go; it will then ascend to the top.

Fig. 32.



To determine the elastic force of the vapour, the height of the column of water or oil must be noted and reduced by calculation to the corresponding value in millimeters of mercury. The elastic force P of the vapour is then found by adding this number to the height of the barometer, and deducting the height of the mercury in the gas-jar above that in the outer cylinder.

By this mode of proceeding we ascertain the volume which a known weight W′ of substance occupies at a given temperature and pressure, and it only remains to determine the weight W of the same volume V of air at the same temperature T and pressure P. This is given in grams by the formula—

$$W = 0{\cdot}0012932\,V \cdot \frac{1}{1 + 0{\cdot}00367\,T} \cdot \frac{P}{760}.$$

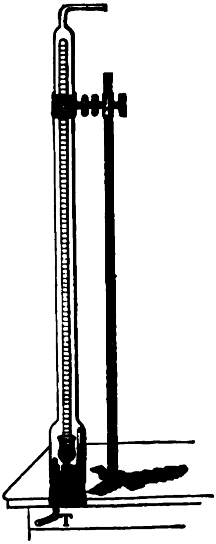
The values of the expression $\frac{1}{1 + 0{\cdot}00367\,T}$ have been calculated by C. Greville Williams for all temperatures from 1° to 150° C. (See Table VIII. in the Appendix; and dividing the weight W′ of the vapour by these values, we obtain, for the density, the expression—

$$D = \frac{W'}{W} = W' \, \frac{1 + 0{\cdot}00367\,T}{0{\cdot}0012932\,V} \cdot \frac{760}{P}.$$

If the gas-jar is graduated in cubic inches and the weights are given in grains, the expression becomes—

$$D = W' \, \frac{1 + 0{\cdot}00367\,T}{0{\cdot}31\,V} \cdot \frac{760}{P}.$$

Fig. 32 *a*.



Of the two methods of determining vapour-densities above described, that of Dumas has the advantage in simplicity of apparatus and facility of execution, especially for high temperatures; indeed, for temperatures above 150° it is the only one that can be employed; but it requires more substance, and does not permit of the density being determined at more than one temperature without making a separate experiment in each case. The process of Gay-Lussac, on the other hand, permits numerous experiments with one small specimen of substance at any desired temperature within certain ranges, and thus enables the operator, in a very short time, to accumulate information regarding certain physical properties of substances which it is often very desirable to know—such, for example, as the lowest temperature at which the substance under study begins to obey the laws of permanent gases.

3. *Hofmann's Method.*—This is a modification of Gay-Lussac's method, devised by Dr A. W. Hofmann (*Deut. Chem. Ges. Ber.* 1868, p. 198) for determining the vapour-densities of high-boiling liquids under reduced pressure, and therefore at comparatively low temperatures.

A graduated glass tube about a meter long and 15 to 20 mm. wide, is filled with mercury and inverted in the little cup A, whereby a barometric vacuum 20 to 30 mm. high is formed at the top. The long tube is enclosed in another tube 30 to 40 mm. wide and 80 to 90 mm. long, drawn out at the top to a conducting tube of moderate width, which is bent at right angles, and connected with a glass or copper vessel in which water, aniline, or other liquid can be boiled. The lower part of the long tube is widened and rests upon a large cork, through which passes an escape-tube T. By this arrangement, a stream of vapour of water, aniline, or other volatile liquid can be made to pass through the space between the two tubes, so as to keep the upper part of the barometer-tube at the temperature required for the determination. The substance whose vapour-density is to be determined, is introduced into the barometric vacuum in small glass tubes fitted with ground stoppers, which are forced out by the tension of the vapour. The great advantage of this method is that, under the very small pressure to which the enclosed vapour is subjected—which may be reduced to 20 or even 10 millimeters of mercury—the determinations may be made at comparatively low temperatures. Thus, in the case of liquids boiling under the ordinary pressure at 120° or even 150°, the vapour-density may be accurately determined at the temperature of boiling water.

Sources of Heat.

The first and greatest source of heat, compared with which all others are totally insignificant, is the sun. The luminous rays are accompanied by heat-rays, which, striking against the surface of the earth, raise its temperature; this heat is communicated to the air by convection, as already described, air and gases in general not being sensibly heated by the passage of the rays.

A second source of heat is supposed to exist in the interior of the earth. It has been observed that, in sinking mine-shafts, boring for water, &c., the temperature rises, in descending, at the rate, it is said, of about 1° F. ($\frac{5}{9}$° C.) for every 45 feet, or 117° F. (65° C.) per mile. On the supposition that the rise continues at the same rate, the earth, at the depth of less than two miles, would have the temperature of boiling water; at nine miles, it would be red-hot; and at thirty or forty miles depth, all known substances would be in a state of fusion.*

According to this idea, the earth must be looked upon as an intensely heated fluid spheroid, covered with a crust of solid badly conducting matter, cooled by radiation into space, and bearing somewhat the same proportion in thickness to the ignited liquid within, that the shell of an egg bears to its fluid contents. Without venturing to offer any opinion on this theory, it may be sufficient to observe that it is not positively at variance with any known fact; that the figure of the earth is really such as would be assumed by a fluid mass; and, lastly, that it offers the best explanation we have of the phenomena of hot springs and volcanic eruptions, and agrees with the chemical nature of their products.

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* The Artesian well at Grenelle, near Paris, has a depth of 1774·5 English feet; it is bored through the chalk basin to the sand beneath. The temperature of the water, which is exceedingly abundant, is 82° F.; the mean temperature of Paris is 51° F.; the difference is 31° F., which gives a rate of about 1° for 58 feet.

Among the other sources of heat are chemical combination and mechanical work.

The disengagement of heat in the act of combination is a phenomena of the utmost generality. The quantity of heat given out in each particular case is fixed and definite; its intensity is dependent upon the time over which the action is extended. Many admirable researches on this subject have been published; but their results will be more advantageously considered at a later part of this work, in connection with the laws of chemical combination.

Heat produced by Mechanical Work.—Heat and motion are convertible one into the other. The powerful mechanical effects produced by the elasticity of the vapour evolved from heated liquids afford abundant illustration of the conversion of heat into motion; and the production of heat by friction, by the hammering of metals, and in the condensation of gases (p. 34), shows with equal clearness that motion may be converted into heat.

In some cases the rise of temperature thus produced appears to be due to a diminution of heat-capacity in the body operated upon, as in the case of a compressed gas just alluded to. Malleable metals, also, as iron and copper, which become heated by hammering or powerful pressure, are found thereby to have their density sensibly increased, and their capacity for heat diminished. A soft iron nail may be made red hot by a few dexterous blows on an anvil; but the experiment cannot be repeated until the metal has been *annealed*, and in that manner restored to its former physical state.

But the amount of heat which can be developed by mechanical force is, in most cases, out of all proportion to what can be accounted for in this way. Sir H. Davy melted two pieces of ice by rubbing them together in a vacuum at the temperature of 0°; and Count Rumford found that the heat developed by the boring of a brass cannon was sufficient to bring to the boiling point two and a half gallons of water, while the dust or shavings of metal cut by the borer weighed only a few ounces. In these and all similar cases the heat appears as a direct result of the force expended; the motion is converted into heat.

The connection between heat and mechanical force appears still more intimate when it is shown that they are related by an exact numerical law, a given quantity of the one being always convertible into a definite amount of the other. The first approximate determination of this most important numerical relation was made by Count Rumford in the manner just alluded to. A brass cylinder enclosed in a box containing a known weight of water at 60° F. was bored by a steel borer made to revolve by horse power, and the time was noted which elapsed before the water was raised to the boiling point by the heat resulting from the friction. In this manner it was found that the heat required to raise the temperature of a pound of water by 1° F. is equivalent to 1034 times the force expended in raising a pound weight one foot high, or to 1034 "foot-pounds," as it is technically expressed. This estimate is now known to be too high, no account having been taken of the heat communicated to the containing vessel, or of that which was lost by dispersion during the experiment.

For the most exact determinations of the mechanical equivalent of heat we are indebted to the careful and elaborate researches of Dr J. P. Joule. From experiments made in the years 1840–43 on the relations between the heat and mechanical power generated by the electric current, Dr Joule was led to conclude that the heat required to raise the temperature of a pound of water 1° F. is equivalent to 838 foot-pounds. This he afterwards reduced to 772; and a nearly equal result was afterwards obtained by experiments on the condensation and rarefaction of gases; but this estimate has since been found to be likewise too great.

The most trustworthy results are obtained by measuring the quantity of heat generated by the friction between solids and liquids. It was for a long time believed that no heat was evolved by the friction of liquids and gases; but in 1842 Meyer showed that the temperature of water may be raised 22° or 23° F. by agitating it. The warmth of the sea after a few days of stormy weather is also probably an effect of fluid friction.

The apparatus employed by Dr Joule for the determination of this important constant, by means of the friction of water, consisted of a brass paddle-wheel furnished with eight sets of revolving vanes, working between four sets of stationary vanes. This revolving apparatus, of which fig. 33 shows a horizontal, and fig. 34 a vertical section, was firmly fitted into a copper vessel (see fig. 35) containing water, in the lid of which were two necks, one for the axis to revolve in without touching, the other for the insertion of a thermometer. A similar apparatus, but made of iron, and of smaller size, having six rotatory and eight sets of stationary vanes, was used for the experiments on the friction of mercury. The apparatus for the friction of cast-iron consisted of a vertical axis carrying a bevelled cast-iron wheel, against which a bevelled wheel was pressed by a lever. The

Fig. 33.

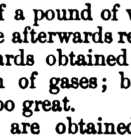
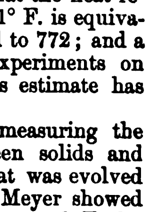
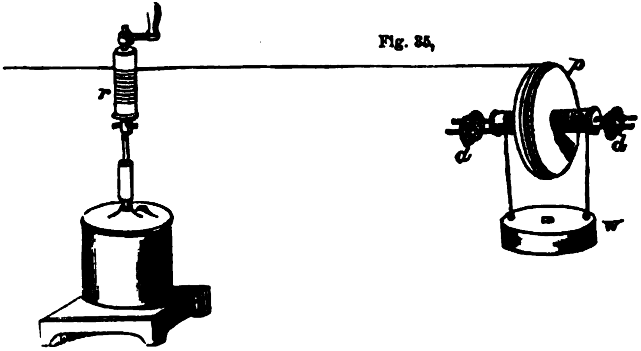


Fig. 34.



wheels were enclosed in a cast-iron vessel filled with mercury, the axis passing through the lid. In each apparatus motion was given to the axis by the descent of leaden weights W (fig. 35) suspended by strings from the axis of two wooden pulleys, one of which is shown at *p*, their axes being supported on friction wheels *d d*, and the pulleys being connected by fine twine with a wooden roller *r*, which, by means of a pin, could be easily attached to or removed from the friction apparatus.

Fig. 35,



The mode of experimenting was as follows:—The temperature of the frictional apparatus having been ascertained, and the weights wound up, the roller was fixed to the axis, and the precise height of the weights ascertained; the roller was then set at liberty, and allowed to revolve till the weights touched the floor. The roller was then detached, the weights wound up again, and the friction renewed. This having been repeated twenty times, the experiment was concluded with another observation of the temperature of the apparatus. The mean temperature of the apartment was ascertained by observations made at the beginning, middle, and end of each experiment. Corrections were made for the effects of radiation and conduction; and, in the experiments with water, for the quantities of heat absorbed by the copper vessel and the paddle-wheel. In the experiments with mercury and cast-iron, the heat-capacity of the entire apparatus was ascertained by observing the heating effect which it produced on a known quantity of water in which it was immersed. In all the experiments, corrections were also made for the velocity with which the weights came to the ground, and for the friction and rigidity of the strings. The thermometers used were capable of indicating a variation of temperature as small as $\frac{1}{200}$ of a degree Fahrenheit.

The following table contains a summary of the results obtained by this method. The second column gives the results as they were obtained in air; in the third column the same results corrected for a vacuum:—

Material employed.	Equivalent in air.	Equivalent in vacuum.	Mean.
Water, . . .	773·640	772·692	772·692
Mercury, . . .	773·762 776·303	772·814 775·352	774·083
Cast-iron, . . .	776·997 774·880	776·045 774·930	774·987

In the experiments with cast-iron, the friction of the wheels produced a considerable vibration of the framework of the apparatus, and a loud sound; it was therefore necessary to make allowance for the quantity of force expended in producing these effects. The number 772·692, obtained by the friction of water, is regarded as the most trustworthy; but even this may be a little too high; because even in the friction of fluids it is impossible entirely to avoid vibration and sound. The conclusions deduced from these experiments are—

1. *That the quantity of heat produced by the friction of bodies, whether solid or liquid, is always proportional to the force expended.*

2. *That the quantity of heat capable of increasing the temperature of* 1 *lb. of water (weighed in vacuo, and between* 55° *and* 60°*) by* 1° *F., requires for its evolution the expenditure of a mechanical force represented by the fall of* 772 *lbs. through the space of* 1 *foot.*

Or, the heat capable of increasing the temperature of 1 *gram of water by* 1° *C., is equivalent to a force represented by the fall of* 423·65 *grams through the space of* 1 *meter. This is consequently the effect of "a unit of heat."*

Experiments made by other philosophers on the work done by a steam-engine, on the heat evolved by an electro-magnetic engine at rest and in motion, and on the heat evolved in the circuit of a voltaic battery and in a metallic wire through which an electric current is passing, have given values for the mechanical equivalent of heat very nearly equal to the above.

Dynamical Theory of Heat.

For a very long time two rival theories have been held regarding the nature of heat: on the one hand, heat has been viewed as having a material existence, though differing from ordinary matter in being without weight, and in other respects; on the other hand, it has been regarded as a state or condition of ordinary matter, and generally as a condition of motion. From the latter part of the last century, until the modern researches upon the mechanical equivalent, the former view had by far the greater number of adherents. Its popularity may be chiefly traced to the teaching of Black and Lavoisier. By the former of these philosophers, the various capacities for heat, or specific heats, of different bodies, seem to have been regarded as analogous to the various proportions of the same acid required to neutralise equal quantities of different bases, while the solid, liquid, and gaseous states were explained by Black as representing so many distinct proportions in which heat was capable of combining with ordinary matter. Very similar views were advocated by Lavoisier: he regarded all gases as compounds of a base characteristic of each, with *caloric*, and supposed that when, as the result of chemical action, they assumed the liquid or solid state, this caloric was set free, and appeared as sensible heat.

Heat was compared by these philosophers to a material substance, in order to explain its then known quantitative relations; and from this point of view the conception introduced by them had the great advantage of being more easily grasped than any which the advocates of the immaterial nature of heat had to offer in its place. It was much easier to conceive of definite quantities of an exceedingly subtile substance or fluid, than of definite quantities of motion, which was itself undefined as to its nature. It was a direct consequence of the material view, that heat should be considered as indestructible and as incapable of being produced, and therefore that the total quantity of heat in the universe should be regarded as at all times the same.

But, on the other hand, this hypothesis did not afford a satisfactory explanation of the production of heat by mechanical means. Here it was not easy to deny the actual generation of heat, or to explain the effects as depending merely on its altered distribution. Nevertheless, the evolution of heat by friction and percussion was generally considered, by the advocates of the material view, as in some way resulting from a diminution in the capacities for heat of the bodies operated upon; and this explanation derived considerable support from the remark, made by Black, that a piece of soft iron, which has been once made red hot by hammering (see p. 60), cannot be so heated a second time until it has been heated to redness in a fire and allowed to cool. In this case, certainly, it seemed as though the hammering forced out heat from the mass of iron, like water from a sponge, and that a fresh supply was taken up when the iron was put in the fire. This explanation, however, did not satisfy Rumford, who, in the investigation described above, made direct experiments upon the specific heat of the chips of metal detached by the friction, and found it to be identical with that of brass under ordinary circumstances. Still more decisive proof that the heat generated by friction cannot be ascribed to a diminution of specific heat in the substances operated on was afforded by Davy's experiment on the liquefaction of ice by friction; for in this case the ice was converted into a liquid having twice the specific heat of the ice itself. Hence Davy* drew the conclusion that, "the immediate cause of the phenomena of heat is motion, and the laws of its communication are precisely the same as the laws of the communication of motion."

The mechanical, or dynamical theory, which regarded heat as consisting in a state of molecular motion, cannot, however, be said to have been definitely established, until it also was made quantitative,—until it was shown that exact numerical laws regulate the production of heat by work or of work by heat, equally with its production during solidification and disappearance during fusion.

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* Elements of Chemical Philosophy, 1812, pp. 94, 95.

To illustrate the general nature of the dynamical theory of heat, we give an outline of the view of the constitution of gases, first put forward, in its present form, by Joule;* and subsequently developed by Krönig,† and Clausius,‡ and of the explanation of the relations existing between solids, liquids, and gases, which has been deduced from it by the last-named philosopher.

First, then, it is assumed that the particles of all bodies are in constant motion, and that this motion constitutes heat, the kind and quantity of motion varying according to the state of the body, whether solid, liquid, or gaseous.

In gases, the molecules—each molecule being an aggregate of atoms—are supposed to be constantly moving forward in straight lines, and with a constant velocity, till they impinge against each other, or against an impenetrable wall. This constant impact of the molecules produces the expansive tendency or elasticity which is the peculiar characteristic of the gaseous state. The rectilinear movement is not, however, the only one with which the particles are affected. For the impact of two molecules, unless it takes place exactly in the line joining their centres of gravity, must give rise to a rotatory motion; and, moreover, the ultimate atoms of which the molecules are composed may be supposed to vibrate within certain limits, being, in fact, thrown into vibration by the impact of the molecules. This vibratory motion is called by Clausius, *the motion of the constituent atoms.* The total quantity of heat in the gas is made up of the progressive motion of the molecules, together with the vibratory and other motions of the constituent atoms; but the progressive motion alone, which is the cause of the expansive tendency, determines the *temperature.* Now, the outward pressure exerted by the gas against the containing envelope arises, according to the hypothesis under consideration, from the impact of a great number of gaseous molecules against the sides of the vessel. But at any given temperature, that is, with any given velocity, the number of such impacts taking place in a given time must vary inversely as the volume of the given quantity of gas: hence *the pressure varies inversely as the volume, or directly as the density,* which is Boyle's law.

When the volume of the gas is constant, the pressure resulting from the impact of the molecules is proportional to the sum of the masses of all the molecules multiplied into the squares of their velocities; in other words, to the so-called *vis viva* or *working force* of the progressive motion. If, for example, the velocity be doubled, each molecule will strike the sides of the vessel with a twofold force, and its number of impacts in a given time will also be doubled: hence the total pressure will be quadrupled.

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* Ann. Ch. Phys. [3] l. 381. † Pogg. Ann. xcix. 315. ‡ Ibid. 353.

Now, we know that when a given quantity of any perfect gas is maintained at a constant volume, it tends to expand by $\frac{1}{273}$ of its bulk at zero for each degree centigrade. Hence the pressure or elastic force increases proportionally to the temperature reckoned from − 273° C.; that is to say, to the absolute temperature. Consequently, *the absolute temperature is proportional to the working force of the progressive motion.*

Moreover, as the motions of the constituent particles of a gas depend on the manner in which its atoms are united, it follows that in any given gas the different motions must be to one another in a constant ratio; and, therefore, the *vis viva* or *working force* of the progressive motion must be an aliquot part of the entire working force of the gas: hence also the absolute temperature is proportional to the total working force arising from all the motions of the particles of the gas.

From this it follows that the quantity of heat which must be added to a gas of constant volume in order to raise its temperature by a given amount, is constant and independent of the temperature. In other words, the specific heat of a gas referred to a given volume is constant, a result which agrees with the experiments of Regnault, mentioned at p. 34. This result may be otherwise expressed, as follows:—*The total* or working *force of the gas is to the working force of the progressive motion of the molecules, which is the measure of the temperature, in a constant ratio.* This ratio is different for different gases, and is greater as the gas is more complex in its constitution; in other words, as its molecules are made up of a greater number of atoms. The specific heat referred to a constant pressure is known to differ from the true specific heat only by a constant quantity.

The relations just considered between the pressure, volume, and temperature of gases, presuppose, however, certain conditions of molecular constitution, which are, perhaps, never rigidly fulfilled: and, accordingly, the experiments of Magnus and Regnault show (p. 31) that gases do exhibit slight deviations from Gay-Lussac and Boyle's laws. What the conditions are which strict adherence to these laws would require, will be better understood by considering the differences of molecular constitution which must exist in the solid, liquid, and gaseous states.

A movement of molecules must be supposed to exist in all three states. In the *solid state*, the motion is such that the molecules oscillate about certain positions of equilibrium, which they do not quit, unless they are acted upon by external forces. This vibratory motion may, however, be of a very complicated character. The constituent atoms of a molecule may vibrate separately, the entire molecules may also vibrate as such about their centres of gravity, and the vibrations may be either rectilinear or rotatory Moreover, when extraneous forces act upon the body, as in shocks, the molecules may permanently alter their relative positions.

In the *liquid state*, the molecules have no determinate positions of equilibrium. They may rotate completely about their centres of gravity, and may also move forward into other positions. But the repulsive action arising from the motion is not strong enough to overcome the mutual attraction of the molecules, and separate them completely from each other. A molecule is not permanently associated with its neighbours, as in the solid state; it does not leave them spontaneously, but only under the influence of forces exerted upon it by other molecules, with which it then comes into the same relation as with the former. There exists, therefore, in the liquid state, a vibratory, rotatory, and progressive movement of the molecules, but so regulated that they are not thereby forced asunder, but remain within a certain volume without exerting any outward pressure.

In the *gaseous* state, on the other hand, the molecules are removed quite beyond the sphere of their mutual attractions, and travel onward in straight lines according to the ordinary laws of motion. When two such molecules meet, they fly apart from each other, for the most part with a velocity equal to that with which they came together. The perfection of the gaseous state, however, implies:—1. That the space actually occupied by the molecules of the gas be infinitely small in comparison with the entire volume of the gas; 2. That the time occupied in the impact of a molecule, either against another molecule or against the sides of the vessel, be infinitely small in comparison with the interval between any two impacts; 3. That the influence of the molecular forces be infinitely small. When these conditions are not completely fulfilled, the gas partakes more or less of the nature of a liquid, and exhibits certain deviations from Gay-Lussac and Boyle's laws. Such is, indeed, the case with all known gases; to a very slight extent with those which have not yet been reduced to the liquid state; but to a greater extent with vapours and condensable gases, especially near the points of condensation.

Let us now return to the consideration of the liquid state. It has been said that the molecule of a liquid, when it leaves those with which it is associated, ultimately takes up a similar position with regard to other molecules. This, however, does not preclude the existence of considerable irregularities in the actual movements. Now, at the surface of the liquid, it may happen that a particle, by a peculiar combination of the rectilinear, rotatory, and vibratory movements, may be projected from the neighbouring molecules with such force as to throw it completely out of their sphere of action, before its projectile velocity can be annihilated by the attractive force which they exert upon it. The molecule will then be driven forward into the space above the liquid, as if it belonged to a gas, and that space, if originally empty, will, in consequence of the action just described, become more and more filled with these projected molecules, which will comport themselves within it exactly like a gas, impinging and exerting pressure upon the sides of the envelope. One of these sides, however, is formed by the surface of the liquid, and when a molecule impinges upon this surface, it will, in general, not be driven back, but retained by the attractive forces of the other molecules. A state of equilibrium, not static, but dynamic, will therefore be attained when the number of molecules projected in a given time into the space above is equal to the number which in the same time impinge upon and are retained by the surface of the liquid. This is the process of vaporisation. The density of the vapour required to ensure the compensation just mentioned, depends upon the rate at which the particles are projected from the surface of the liquid, and this again upon the rapidity of their movement within the liquid, that is to say, upon the temperature. It is clear, therefore, that the density of a saturated vapour must increase with the temperature.

If the space above the liquid is previously filled with a gas, the molecules of this gas will impinge upon the surface of the liquid, and thereby exert pressure upon it; but as these gas-molecules occupy but an extremely small proportion of the space above the liquid, the particles of the liquid will be projected into that space almost as if it were empty. In the middle of the liquid, however, the external pressure of the gas acts in a different manner. There also it may happen that the molecules may be separated with such force as to produce a small vacuum in the midst of the liquid. But this space is surrounded on all sides by masses which afford no passage to the disturbed molecules; and in order that they may increase to a permanent vapour-bubble, the number of molecules projected from the inner surface of the vessel must be such as to produce a pressure outwards equal to the external pressure tending to compress the vapour-bubble. The boiling of the liquid will, therefore, be higher as the external pressure is greater.

According to this view of the process of vaporisation, it is possible that vapour may rise from a solid as well as from a liquid; but it by no means necessarily follows that vapour must be formed from all bodies at all temperatures. The force which holds together the molecules of a body may be too great to be overcome by any combination of molecular movements, so long as the temperature does not exceed a certain limit.

The *production* and *consumption of heat* which accompany changes in the state of aggregation, or of the volume of bodies, are easily explained, according to the preceding principles, by taking account of the *work* done by the acting forces. This work is partly *external* to the body, partly *internal*. To consider first the *internal* work:

When the molecules of a body change their relative positions, the change may take place either in accordance with or in opposition to the action of the molecular forces existing within the body. In the former case, the molecules, during the passage from one state to the other, have a certain velocity imparted to them, which is immediately converted into heat; in the latter case, the velocity of their movement, and consequently the temperature of the body, is diminished. In the passage from the solid to the liquid state, the molecules, although not removed from the spheres of their mutual attractions, nevertheless change their relative positions in opposition to the molecular forces, which forces have, therefore, to be overcome. In evaporation, a certain number of the molecules are completely separated from the remainder, which again implies the overcoming of opposing forces. In both cases, therefore, work is done, and a certain portion of the working force of the molecules, that is, of the heat of the body, is lost. But when once the perfect gaseous state is attained, the molecular forces are completely overcome, and any further expansion may take place without internal work, and, therefore, without loss of heat, provided there is no external resistance.

But in nearly all cases of change of state or volume, there is a certain amount of external resistance to be overcome, and a corresponding loss of heat. When the pressure of a gas, that is to say, the impact of its atoms, is exerted against a movable obstacle, such as a piston, the molecules lose just as much of their moving power as they have imparted to the piston, and, consequently, their velocity is diminished and the temperature lowered. On the contrary, when a gas is compressed by the motion of a piston, its molecules are driven back with greater velocity than that with which they impinged on the piston, and, consequently, the temperature of the gas is raised.

When a liquid is converted into vapour, the molecules have to overcome the atmospheric pressure or other external resistance, and, in consequence of this, together with the internal work already spoken of, a large quantity of heat disappears, or is rendered *latent*, the quantity thus consumed being, to a considerable extent, affected by the external pressure. The liquefaction of a solid not being attended with much increase of volume, involves but little external work; nevertheless the atmospheric pressure does influence, to a slight amount, both the latent heat of fusion and the melting point.

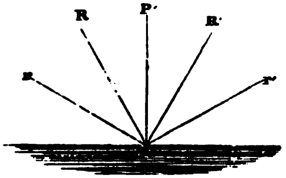
LIGHT.

Two views have been entertained respecting the nature of light. Newton imagined that luminous bodies emit, or shoot out, infinitely small particles in straight lines, which, by penetrating the transparent parts of the eye and falling upon the nervous tissue, produce vision. Other philosphers drew a parallel between the properties of light and those of sound, and considered that, as sound is certainly the effect of undulations, or little waves, propagated through elastic bodies in all directions, so light might be nothing more than the consequence of similar undulations transmitted with inconceivable velocity through a highly elastic medium, of excessive tenuity, filling all space, and occupying the intervals between the particles of material substances. To this medium they gave the name of *ether*. The wave hypothesis of light is at present generally adopted. It is in harmony with all the known phenomena discovered since the time of Newton, not a few of which were first deduced from the undulatory theory, and afterwards verified by experiment. Several well-known facts are in direct opposition to the theory of emission.

A ray of light emitted from a luminous body proceeds in a straight line, and with extreme velocity. Certain astronomical observations afford the means of approximating to a knowledge of this velocity. The satellites of Jupiter revolve about the planet in the same manner as the moon about the earth, and the time of revolution of each satellite is exactly known from its periodical entry into or exit from the shadow of the planet. The time required by one is only 42 hours. Römer, the astronomer of Copenhagen, found that this period appeared to be longer when the earth, in its passage round the sun, moved from the planet Jupiter; and, on the contrary, he observed that the periodic time appeared to be shorter when the earth moved in the direction towards Jupiter. The difference, though very small for a single revolution of the satellite, increases, by the addition of many revolutions, during the passage of the earth from its nearest to its greatest distance from Jupiter, that is, in about half a year, till it amounts to 16 minutes and 16 seconds. Römer concluded from this, that the light of the sun, reflected from the satellite, required that time to pass through a distance equal to the diameter of the orbit of the earth; and since this space is little short of 200 millions of miles, the velocity of light cannot be less than 200,000 miles in a second of time. It will be seen hereafter that this rapidity of transmission is rivalled by that of electricity. Another astronomical phenomenon, observed and correctly explained by Bradley, the aberration of the fixed stars, leads to the same result. Physicists have, moreover, succeeded in measuring the velocity of light for terrestrial, and indeed comparatively small distances; the results of these experiments essentially correspond with those given by astronomical observations.

REFLECTION.—When a ray of light falls upon a boundary between two media, a part of it, and, in exceptional cases, the whole, is reflected into the first medium, whilst the other part penetrates into the second medium.

Fig. 36.



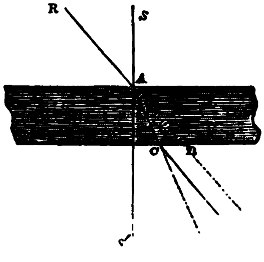
The law of regular reflection is extremely simple. If a line be drawn perpendicular to the surface upon which the ray falls, and the angle contained between the ray and the perpendicular be measured, it will be found that the ray, after reflection, takes such a course as to make with the perpendicular an equal angle on the opposite side of the latter. A ray of light, R, falling at the point P, will be reflected in the direction PR′, making the angle R′PP′ equal to the angle RPP′; and a ray from the point *r* falling upon the same spot will be reflected to *r′* in virtue of the same law. Further, it is to be observed, that the incident and reflected rays are always contained in the same normal plane.

The same rule holds good if the mirror be curved, as a portion of a sphere, the curve being considered as made up of a multitude of little planes. Parallel rays cease to be so when reflected from curved surfaces, becoming divergent or convergent according as the reflecting surface is convex or concave.

Bodies with rough and uneven surfaces, the smallest parts of which are inclined towards each other without order, reflect the light diffused. The perception of bodies depends upon the diffused reflected light.

REFRACTION.—It has just been stated that light passes in straight lines; but this is true only so long as the medium through which it travels preserves the same density and the same chemical nature: when this ceases to be the case, the ray of light is bent from its course into a new one, or is said to be *refracted*.

Fig. 37.

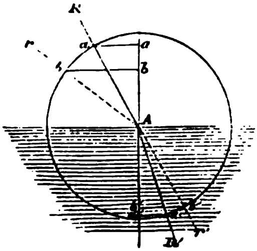


Let R (fig. 37) be a ray of light falling upon a plate of some transparent substance with parallel sides, such as a piece of thick plate glass,—in short, any transparent homogeneous material which is either non-crystalline, or crystallises in the regular system; and let A be its point of contact with the upper surface. The ray, instead of holding a straight course and passing into the glass in the direction A B, will be bent downwards to C; and, on leaving the glass, and issuing into the air on the other side, it will again be bent, but in the opposite direction, so as to make it parallel to the continuation of its former track, provided there be one and the same medium on the upper and lower side of the plate. The general law is thus expressed :—When the ray passes from a rare to a denser medium, it is usually refracted *towards* a line perpendicular to the surface of the latter; and conversely, when it leaves a dense medium for a rarer one, it is refracted *from* a line perpendicular to the surface of the denser substance; in the former case the angle of incidence is greater than that of refraction; in the latter, it is less. In both cases the direction of the refracted ray is in the plane R A S, which is formed by the falling ray and the perpendicular S A drawn from the spot where the ray is refracted; the angle R A S = B A S′, is called the angle of incidence. The angle C A S′ is called the angle of refraction. The difference of these two angles, that is, the angle C A B, is the refraction.

The amount of refraction, for the same medium, varies with the obliquity with which the ray strikes the surface. When perpendicular to the latter, the ray passes without change of direction at all; and in other positions, the refraction increases with the obliquity.

Let R (fig. 38) represent a ray of light falling upon the surface of a mass of plate glass at the point A. From this point let a perpendicular fall and be continued into the new medium, and around the same point, as a centre, let a circle be drawn. According to the law just stated, the refraction must be towards the perpendicular; in the direction A R′, for example. Let the lines *a*—*a*, *a′*—*a′*, at right angles to the perpendicular, be drawn, and their length compared by means of a scale of equal parts, and noted: their length will, in the case supposed, be in proportion of 3 to 2. These lines are termed the *sines* of the angles of incidence and refraction respectively.

Fig. 38.



Now let another ray be taken, such as *r*; it is refracted in the same manner to *r′*, the bending being greater from the increased obliquity of the ray; but what is very remarkable, if the sines of the two new angles of incidence and refraction be again compared, they will still be found to bear to each other the proportion of 3 to 2. The fact is expressed by saying, that so long as the light passes from one to the other of the same two media, the *ratio of the sines of the angles of incidence and refraction is constant.* This ratio is called the *index of refraction.*

Different bodies possess different refractive powers; generally speaking, the densest substances refract most. Combustible bodies have been noticed to possess greater refractive power than their density would indicate, and from this observation Newton predicted the combustible nature of the diamond long before anything was known respecting its chemical nature.

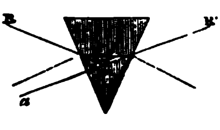
The method adopted for describing the comparative refractive power of different bodies, is to state the ratio borne by the sine of the angle of incidence in the first medium at the boundary of the second, to the sine of the angle of refraction in this second medium; this is called the *index of refraction* of the two substances; it is greater or less than unity, according as the second medium is denser or rarer than the first. In the case of air and plate glass the index of refraction is 1·5.

When the index of refraction of any particular substance is once known, the effect of the latter upon a ray of light entering it in any position can be calculated by the law of sines. The following table exhibits the indices of refraction of several substances, supposing the ray to pass into them from the air:—

Substances.	Index of refraction.	Substances.	Index of refraction.
Tabasheer,*	1·10	Garnet,	1·80
Ice,	1·30	Glass with much oxide of lead,	1·90
Water,	1·34	Zircon,	2·00
Fluor spar,	1·40	Phosphorus,	2·20
Plate glass,	1·50	Diamond,	2·50
Rock-crystal,	1·60	Chromate of lead,	3·00
Chrysolite,	1·69	Cinnabar,	3·20
Bisulphide of carbon,	1·70		

When a luminous ray enters a mass of substance differing in refractive power from the air, and whose surfaces are not parallel, it becomes permanently deflected from its course and altered in its direction. It is upon this principle that the properties of prisms and lenses depend. To take an example.—Figure 39 represents a triangular prism of glass, upon the side of which the ray of light R may be supposed to fall. This ray will of course be refracted, on entering the glass, towards a line perpendicular to the first surface, and again, from a line perpendicular to the second surface on emerging into the air. The result is the deflection *a c* R, which is equal to the sum of the two deflections which the ray undergoes in passing through the prism.

Fig. 39.



A convex lens is thus enabled to converge rays of light falling upon it, and a concave lens to separate them more widely; each separate part of the surface of the lens producing its own independent effect.

DISPERSION.—The light of the sun and celestial bodies in general, as well as that of the electric spark and of all ordinary flames, is

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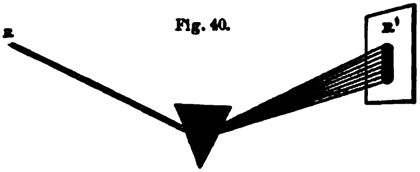
[*] A siliceous deposit in the joints of the bamboo.

of a compound nature. If a ray of light from any of the sources mentioned be admitted into a dark room by a small hole in a shutter, or otherwise, and suffered to fall upon a glass prism, in the manner shown in fig. 40, it will not only be refracted from its straight course, but will be decomposed into a number of coloured rays, which may be received upon a white screen placed behind the prism. When solar light is employed, the colours are extremely brilliant, and spread into an oblong space of considerable length.

Fig. 40.



The prism being placed with its base upwards, as in fig. 40, the upper part of this image, or *spectrum*, will be violet and the lower red, the intermediate portion, commencing from the violet, being indigo, blue, green, yellow, and orange, all graduating imperceptibly into each other. This is the celebrated experiment of Sir Isaac Newton; from it he drew the inference that white light is composed of seven primitive colours, the rays of which are differently refrangible by the same medium, and hence capable of being thus separated. The violet rays are most refrangible, and the red rays least.*

Bodies of the same mean refractive power do not always equally disperse or spread out the differently coloured rays to the same extent; because the principal yellow or red rays, for instance, are equally refracted by two prisms of different materials, it does not follow that the blue or the violet will be similarly affected. Hence, prisms of different varieties of glass, or other transparent substances, give, under similar circumstances, very different spectra, both as respects the length of the image, and the relative extent of the coloured bands.

The appearance of the spectrum may also vary with the nature of the source of light: the investigation of these differences, however, involves the use of a more delicate apparatus. Fig. 41 shows the principle of such an apparatus, which is called a *spectroscope.*

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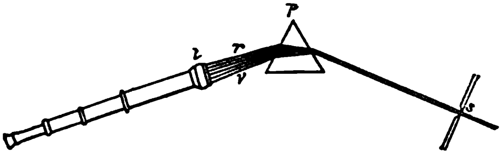
* The colours of natural objects are supposed to result from the power possessed by their surfaces of absorbing some of the coloured rays, while they reflect or transmit, as the case may be, the remainder of the rays. Thus an object appears red because it absorbs or causes to disappear the yellow and blue rays composing the white light by which it is illuminated. Any colour which remains after the deduction of another colour from white light, is said to be *complementary* to the latter. Complementary colours, when acting simultaneously, reproduce white light. Thus in the example already quoted, red and green are complementary colours. The fact of complementary colours giving rise to white light may be readily illustrated by mixing in appropriate quantities a rose-red solution of cobalt and green solution of nickel; the resulting liquid is nearly colourless.

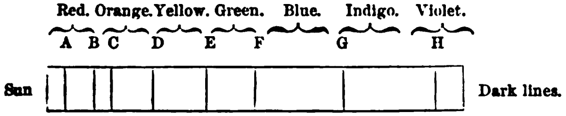
Fig. 41.



The light, passing through a fine slit, *s*, impinges upon a flint-glass prism, *p*, by which it is dispersed. The decomposed light emerges from the prism in several directions between *r* (red rays) and *v* (violet rays); and the spectrum thus produced is observed by the telescope *t*, which receives only part of it at once; but the several parts may be readily examined by turning slightly either the prism or the telescope.

If the solar spectrum be examined in this manner, numerous dark lines parallel with the edge of the prism are observed. They were discovered in 1802 by Dr Wollaston, and subsequently more minutely investigated by Fraunhofer. They are generally known as Fraunhofer's lines. These dark lines, which exist in great numbers, and of very varying strength, are irregularly distributed over the whole spectrum. Some of them, in consequence of their peculiar strength and their relative position, may always be easily recognised; the more conspicuous are represented in fig. 42, and in the frontispiece. The same dark lines, though paler, and much more difficult to recognise, are observed in the spectrum of planets lighted by the sun; for instance, in the light emanating from Venus. On the other hand, the dark lines observed in the spectra which are produced by the light emanating from fixed stars—from Sirius, for instance—differ in position from those previously mentioned.

Fig. 42.

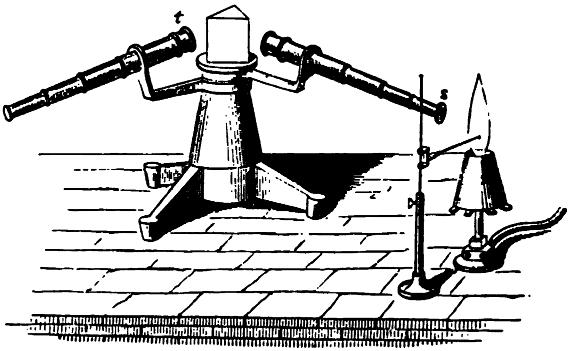


Sources of light which contain no volatile constitutents—incandescent platinum wire, for example—furnish continuous spectra, exhibiting no such lines. But if volatile substances be present in the source of light, bright lines are observed in the spectrum, which are frequently characteristic of the volatile substances.

Professor Plücker, of Bonn, has investigated the spectra which are produced by the electric light when developed in very rarefied gases. He found the bright lines and the dark stripes between the lines varying considerably with different gases. When the electric light was developed in a mixture of two gases, the spectrum thus obtained exhibited simultaneously the peculiar spectra belonging to the two gases of which the mixture consisted. When the experiment was made in gaseous compounds capable of being decomposed by the electric current, this decomposition was indicated by the spectra of the separated constitutents becoming perceptible.

Many years ago the spectra of coloured flames were examined by Sir John Herschel, Fox Talbot, and W. A. Miller. Within the last few years results of the greatest importance have been obtained by Kirchhoff and Bunsen, who have investigated the spectra furnished by the incandescence of volatile substances: these reseaches have enriched chemistry with a new method of analysis, the analysis by spectrum observations. In order to recognise one of the metals of the alkalis or of the alkaline earths, it is generally sufficient to introduce a minute quantity of a moderately volatile compound of the metal, on the loop of a platinum wire, into the edge of the very hot, but scarcely luminous flame, of a mixture of air and coal-gas, and to examine the spectrum which is furnished by the flame containing the vapour of the metal or its compound. Fig. 43 exhibits the apparatus which is used in performing experiments of this description. The light of the flame in which the metallic compound is evaporated passes through the fine slit in the disc, *s*, into a tube, the opposite end of which is provided with a convex lens. This lens collects the rays diverging from the slit, and throws them parallel upon the prism, *p*. The light is decomposed by the prism, and the spectrum thus obtained is observed by means of the telescope,

Fig. 43.



which may be turned round the axis of the stand carrying the prism. Foreign light is excluded by an appropriate covering.

The limits of this elementary treatise do not permit us to describe the ingenious arrangements which have been contrived for sending the light from different sources through the same prism at different heights, whereby their spectra, the solar spectrum, for instance, and that of a flame, may be placed in a parallel position, the one above the other, and thus be compared.* The spectra of flames in which different substances are volatilised frequently exhibit such characteristically distinct phenomena, that they may be used with the greatest advantage for the discrimination of these substances. Thus the spectrum of a flame containing sodium (Na) exhibits a bright line on the yellow portion, the spectrum of potassium (K) a characteristic bright line at the extreme limit of the red, and another at the opposite violet limit of the spectrum. Lithium (Li) shows a bright brilliant line in the red, and a paler line in the yellow portion ; strontium (Sr) a bright line in the blue, one in the orange, and six less distinct ones in the red portion of the spectrum. The frontispiece exhibits the most remarkable of the dark lines of the solar spectrum (Fraunhofer's lines), and the position of the bright lines in the spectra of flames containing the vapours of compounds of the metals of the alkalis and alkaline earths, also of the metals thallium and indium.

The delicacy of these spectral reactions is very considerable, but unequal in the case of different metals. The presence of $\frac{1}{200,000,000}$ grain of sodium in the flame is still easily recognisable by the bright yellow line in the spectrum. Lithium, when introduced in the form of a volatile compound, imparts to the flame a red colour ; but this coloration is no longer perceptible when a volatile sodium compound is simultaneously present, the yellow coloration of the flame predominating under such circumstances. But when a mixture of one part of lithium and 1000 parts of sodium is volatilised in a flame, the spectrum of the flame exhibits, together with the bright yellow sodium line, likewise the red line characteristic of lithium. The observation of bright lines not belonging to any of the previously known bodies has led to the discovery of new elements. Thus, Bunsen and Kirchhoff, when examining the spectrum of a flame in which a mixture of alkaline salt was evaporated, observed some bright lines, which could not be attributed to any of the known elements, and were thus led to the discovery of the two new metals, cæsium and rubidium. By the same method a new element, thallium, has been more recently discovered by Mr Crookes; another, called indium, by Reich and Richter; and a third, called gallium, by Lecoq de Boisbaudran.

For the examination of the bright lines in the spectra of metals, the electric spark, passing between two points of the metal under examination, may be conveniently employed as a source of light. Small quantities of the metal are invariably volatilised; and the spectrum developed by the electric light exhibits the bright lines characteristic of the metal employed. These lines were observed by Wheatstone as early as 1835. This method of investigation is more especially applicable to the examination of the spectra of the heavy metals.

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* See the article "Spectral Analysis," by Prof. Roscoe, in Watts's Dictionary of Chemistry, vol. v.

By a series of theoretical considerations, Professor Kirchhoff has arrived at the conclusion that the spectrum of an incandescent gas is reversed—*i.e.*, that the bright lines become dark lines—if there be behind the incandescent gas a very luminous source of light, which by itself furnishes a continuous spectrum. Kirchhoff and Bunsen have fully confirmed this conclusion by experiment. Thus a volatile lithium salt produces, as just pointed out, a very distinct bright line in the red portion of the spectrum; but if bright sunlight, or the light emitted by a solid body heated to the most powerful incandescence, be allowed to fall through the flame upon the prism, the spectrum exhibits, in the place of this bright line, a black line similar in every respect to Fraunhofer's lines in the solar spectrum. In like manner the bright strontium line is reversed into a dark line. Kirchhoff and Bunsen have expressed the opinion that all the Fraunhofer lines in the solar spectrum are bright lines thus reversed. In their conception, the sun is surrounded by a luminous atmosphere, containing a certain number of volatilised substances, which would give rise in the spectrum to certain bright lines, if the light of the solar atmosphere alone could reach the prism; but the intense light of the powerfully incandescent body of the sun which passes through the solar atmosphere, causes these bright lines to be reversed and to appear as dark lines on the ordinary solar spectrum. Kirchhoff and Bunsen have thus been enabled to attempt the investigation of the chemical constitutents of the solar atmosphere, by ascertaining the elements which, when in the state of incandescent vapour, develop bright spectral lines, coinciding with Fraunhofer's lines in the solar spectrum. Fraunhofer's line D (fig. 42) coincides most accurately with the bright spectral line of sodium, and may be artificially produced by reversing the latter; sodium would thus appear to be a constituent of the solar atmosphere. Kirchhoff has proved, moreover, that sixty bright lines perceptible in the spectrum of iron correspond, both as to position and distinction, most exactly with the same number of dark lines in the solar spectrum, and, accordingly, he believes iron, in the state of vapour, to be present in the solar atmosphere. In a similar manner this physicist has endeavoured to establish the presence of several other elements in the solar atmosphere.

Absorption Spectra.—The relative quantities of the several coloured rays absorbed by a coloured medium of given thickness may be observed by viewing a line of light through a prism and the coloured medium; the spectrum will then be seen to be diminished in brightness in some parts, and perhaps cut off altogether in others. This mode of observation is often of great use in chemical analysis, as many coloured substances when thus examined afford very characteristic spectra, the peculiarities of which may often be distinguished, even though the solution of the substance under examination contains a sufficient amount of coloured impurities to change its colour very considerably. The following method of making the observation is given by Professor Stokes.*

A small prism is to be chosen of dense flint glass, ground to an angle of 60°, and just large enough to cover the eye comfortably. The top and bottom should be flat, for convenience of holding the prism between the thumb and fore-finger, and laying it down on a table, so as not to scratch or soil the faces. A fine line of light is obtained by making a vertical slit in a board six inches square, or a little longer in a horizontal direction, and adapting to the aperture two pieces of thin metal. One of the metal pieces is movable, to allow of altering the breadth of the slit. About the fiftieth of an inch is a suitable breadth for ordinary purposes. The board and metal pieces should be well blackened.

On holding the board at arm's length against the sky or a luminous flame, the slit being, we will suppose, in a vertical direction, and viewing the line of light thus formed through the prism held close to the eye, with its edge vertical, a pure spectrum is obtained at a proper azimuth of the prism. Turning the prism round its axis alters the focus, and the proper focus is got by trial. The whole of the spectrum is not, indeed, in perfect focus at once, so that in scrutinising one part after another, it is requisite to turn the prism a little. When daylight is used, the spectrum is known to be pure by its showing the principal fixed lines; in other cases the focus is got by the condition of seeing distinctly the other objects, whatever they may be, which are presented in the spectrum. To observe the absorption spectrum of a liquid, an elastic band is put round the board near the top, and a test-tube containing the liquid is slipped under the band, which holds it in its place behind the slit. The spectrum is then observed just as before, the test-tube being turned from the eye.

To observe the whole progress of the absorption, different degrees of strength must be used in succession, beginning with a strength which does not render any part of the spectrum absolutely black, unless it be one or more very narrow bands, as otherwise the most distinctive features of the absorption might be missed. If the solution be contained in a wedge-shaped vessel instead of a test-tube, the progress of the absorption may be watched in a continuous manner by sliding the vessel before the eye. Some observers prefer using a wedge-shaped vessel in combination with the slit, the slit being perpendicular to the edge of the wedge. In this case each element of the slit forms an elementary spectrum corresponding with a thickness of the solution which increases in a continuous manner from the edge of the wedge, where it vanishes. This is the mode of observation adopted by Gladstone.*

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* Chem. Soc. Journ. xvii. 306.

Fig. 44 represents the effect produced in this way by a solution of chromic chloride, and fig. 45 that produced by a solution of potassium permanganate.

Fig. 44.

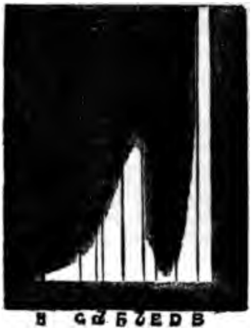
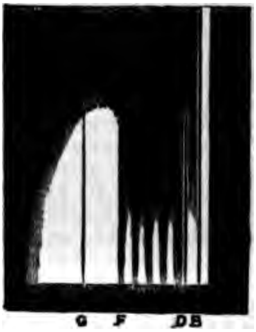


Fig. 45.



The right hand side of these figures corresponds with the red end of the spectrum; the letters refer to Fraunhofer's lines. The lower part of each figure shows the pure spectrum seen through the thinnest part of the wedge; and the progress of the absorption, as the thickness of the liquid increases, is seen by the gradual obliteration of the spectrum towards the upper part of the figures.

Fluorescence.—An examination into a peculiar mode of analysis of light, discovered by Sir John Herschel, in a solution of quinine sulphate, has within the last few years led to the discovery of a most remarkable fact. Professor Stokes has observed that light of certain refrangibility and colour is capable of experiencing a peculiar influence in being dispersed by certain media, and of undergoing thereby an alteration of its refrangibility and colour. This curious change, called fluorescence, can be produced by a great number of bodies, both liquid and solid, transparent and opaque. Frequently the change affects only the extreme limits; at other times larger portions; and in a few cases even the whole, or, at all events, the major part of the spectrum. A dilute solution of quinine sulphate, for instance, changes the violet and the dark-blue light to sky-blue; by a decoction of madder in a solution of alum all rays of higher refrangibility than yellow are converted into yellow; by an alcoholic solution of the colouring matter of leaves, all the rays of the spectrum become red. In all cases in which this peculiar phenomenon presented itself in a greater or less degree, Mr Stokes observed that it consisted in a diminution of the refrangibility. Thus, rays of so high a degree of refrangibility, that they extend far beyond the extreme limits of the spectrum visible under ordinary circumstances, may be rendered luminous, and converted into blue and even red light.

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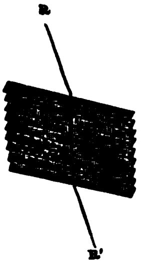
* Chem. Soc. Journ. x. 79.

Double Refraction and Polarisation.—A ray of common light made to pass through certain crystals of a particular order is found to undergo a very remarkable change. It becomes split or divided into two rays, one of which follows the general law of refraction, while the other takes a new and extraordinary course, dependent on the position of the crystal. This effect, which is called double refraction, is beautifully illustrated in the case of Iceland spar, or crystallised calcium carbonate. On placing a rhomb of this substance on a piece of white paper on which a mark or line has been made, the object will be seen double.

Again, if a ray of light be suffered to fall on a plate of glass at an angle of 56° 45′, the portion of the ray which suffers reflection will be found to have acquired properties which it did not before possess; for on throwing it, at the same angle, upon a second glass plate, it will be observed that there are two particular positions of the latter, namely, those in which the planes of incidence are at right angles to one another, when the ray of light is no longer reflected, but entirely refracted. Light which has suffered this change is said to be *polarised.*

Fig. 46.



The light which passes through the first or polarising plate is also, to a certain extent, in this peculiar condition, and by employing a series of similar plates held parallel to the first, this effect may be greatly increased; a bundle of fifteen or twenty such plates may be used with great convenience for the experiment. It is to be remarked, also, that the light polarised by transmission in this manner is in an opposite state to that polarised by reflection; that is, when examined by a second or *analysing* plate, held at the angle before mentioned, it will be seen to be reflected when the other is transmitted, and to be dispersed when the first is reflected.

It is not every substance that is capable of polarising light in this manner; glass, water, and certain other bodies bring about the change in question, each having a particular polarising angle at which the effect is greatest. For each transparent substance the polarising angle is that at which the reflected and refracted rays are perpendicular to each other. Metals can also polarise light, by reflection, but they do so very imperfectly.

The two rays into which a pencil of common light divides itself in passing through a doubly-refracting crystal are found on examination to be polarised in a very complete manner, and also transversely, the one being capable of reflection when the other vanishes or is transmitted. The two rays are said to be polarised in opposite directions. With a rhomb of transparent Iceland spar of tolerably large dimensions, the two oppositely polarised rays may be widely separated and examined apart.

Certain doubly refracting crystals absorb one of these rays, but not the other. Through a plate of such a crystal one ray passes and becomes entirely polarised; the other, which is likewise polarised, but in another plane, is removed by absorption. The best known of these media is tourmaline. When two plates of this mineral, cut parallel to the axis of the crystal, are held with their axes parallel, as in fig. 47, light traverses them both freely; but when one of them is turned round in the manner shown in fig. 48 so as to make the axes cross at right angles, the light is almost wholly stopped, if the tourmalines are good. A plate of the mineral thus becomes an excellent test for discriminating between polarised light and that which has not undergone the change.

Fig. 47.

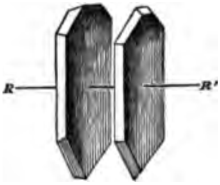
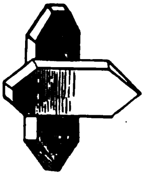


Fig. 48.



Instead of the tourmaline plate, which is always coloured, frequent use is made of two Nichol's prisms, or conjoined prisms of calcium carbonate, which, in consequence of a peculiar cutting and combination, possess the property of allowing only one of the oppositely polarised rays to pass. A more advantageous method of cutting and combining prisms has been given by M. Foucault. His prisms are as serviceable as, and less expensive than, those of Nichol. If two Nichol's or Foucault's prisms be placed one behind the other in precisely similar positions, the light polarised by the one goes through the other unaltered. But when one prism is slightly turned round in its setting, a cloudiness is produced; and by continuing to turn the prism, this increases until perfect darkness ensues. This happens, as with the tourmaline plates, when the two prisms cross one another. The phenomenon is the same with colourless as with coloured light.

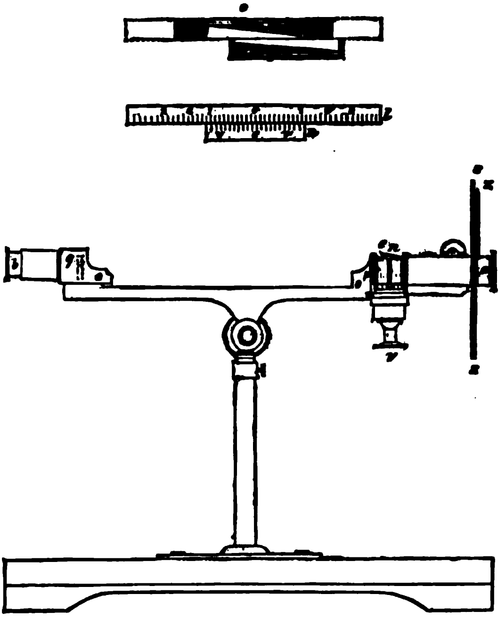
Circular Polarisation.—Supposing that polarised light, coloured, for example, by going through a plate of red glass, has passed through the first Nichol's prism, and been altogether obstructed in consequence of the position of the second prism, then, if between the two prisms a plate of rock-crystal, formed by a section at right angles to the principal axis of the crystal, be interposed, the light polarised by the first prism will, by passing through the plate of quartz, be enabled partially to pass through the second Nichol's prisms. Its passage through the second prism can then again be interrupted by turning the second prism round to a certain extent. The rotation required varies with the thickness of the plate of rock-crystal, and with the colour of the light employed. It increases from red in the following order—yellow, green, blue, violet.

This property of rock-crystal was discovered by Arago. The kind of polarisation has been called circular polarisation. The direction of the rotation is with many plates towards the right hand; in other plates it is towards the left. The one class is said to possess right-handed polarisation, or to be *dextrorotatory* or *dextrogyrate;* the other to possesss class left-handed polarisation, or to be *levorotatory* or *levogyrate.* For a long time quartz was the only solid body known to exhibit circular polarisation. Others have since been found which possess this property in a far higher degree. Thus, a plate of cinnabar acts fifteen times more powerfully than a plate of quartz of equal thickness.

Biot observed that many solutions of organic substances exhibit the property of circular polarisation, though to a far less extent than rock-crystal. Thus, solutions of cane-sugar, glucose, and tartaric acid, possess right-handed polarisation; whilst albumin, uncrystallisable sugar, and oil of turpentine, are left-handed. In all these solutions the amount of circular polarisation increases with the concentration of the liquid, and the thickness of the column through which the light passes. Hence circular polarisation is an important auxiliary in chemical analysis. In order to determine the amount of polarisation which any liquid exhibits, it is put into a glass tube not less than from ten to twelve inches long, which is closed with glass plates. This is then placed between the two Nichol's prisms, which have previously been so arranged with regard to each other that no light could pass through. An apparatus of this description, the saccharimeter, is used for determining the concentration of solutions of cane-sugar.

The form of this instrument is shown in fig. 49. The two Nichol's prisms are enclosed in the corresponding fastenings *a* and *b*. Between the two there is a space to receive the tube, which is filled with the solution of sugar. If the prisms are crossed in the way above mentioned before the tube is put in its place, that is, if they are placed so that no light passes them, then, by the action of the solution of sugar, the light is enabled to pass, and the Nichol's prism, *a*, must be turned through a certain angle before the light is again perfectly stopped. The magnitude of this angle is observed on the circular disk *s s*, which is divided into degrees, and upon which, by the turning of the prism, an index *z* is moved along the division. When the tube is exactly ten inches long, and closed at both ends by flat glass plates, and when it is filled with solution containing 10 per cent. by weight of cane-sugar, and free from any other substance possessing an action on light, the angle of rotation for the middle yellow ray is 19·6°. Now, the magnitude of this angle is directly proportional to the length of the column of liquid, and also to the quantity of sugar in solution. If, therefore, a solution containing z per cent. by weight of sugar in a tube l inches long, produce a rotation equal to a degrees, the percentage of sugar will be given by the equation—

Fig. 49.



$$\frac{a}{19{\cdot}6} = \frac{l}{10} \cdot \frac{z}{10},$$

whence

$$z = \frac{100\,a}{19{\cdot}6\,l}.$$

This process is not sufficient when the solution contains cane-sugar and uncrystallisable sugar; for the latter rotates the ray to the left; in that case only the difference of the two actions is obtained. But if the whole quantity of sugar be changed into uncrystallisable sugar, and the experiment be repeated, then from the results of the two observations the quantity of both kinds of sugar can easily be calculated.

It is difficult to find exactly that position of the Nichol's prisms in which the greatest darkness prevails. To make the measurements more exact and easy, Soleil has made some additions to the apparatus. At *q*, before the prism *b*, a plate of rock-crystal cut at right angles to the axis is placed. It is divided in the centre of the field of vision, half consisting of quartz rotating to the right hand, and half of the variety which rotates to the left; it is 0·148 inch (3·75 millimeters,) thick, this thickness being found by experiment to produce the greatest difference in the colour of the two halves, when one prism is slightly rotated. The solution of sugar has precisely the same action on the rotation, since it increases the action of the half which has a right-handed rotation, and lessens the action of the half which rotates to the left. Hence the two halves will assume a different colour when the smallest quantity of sugar is present in the liquid. By slightly turning the Nichol's prism *a*, this difference can be again removed. Soleil has introduced another more delicate means of effecting this, at the part *l*, which he calls the compensator. The most important parts of this are separately represented in fig. 49. It consists of two exactly equal right-angled prisms, of left-handed quartz, whose surfaces, *c* and *c′*, are cut perpendicular to the optic axis. These prisms can, by means of the screw *v* and a rack and pinion, be made to slide on one another, so that, when taken together, they form a plate of varying thickness, bounded by parallel surfaces. One of the frames has a scale *l*, the other a vernier *n*. When this points to zero of the scale, the optical action of the two prisms is exactly compensated by a right-handed plate of rock-crystal, so that an effect is obtained as regards circular polarisation, as if the whole system were not present. As soon, however, as the screw is moved, and thus the thickness of the plate formed by the two prisms is changed (we will suppose it increased), then a left-handed action ensues, which must be properly regulated, until it compensates the opposite action of a solution of sugar. Thus a convenient method is obtained of rendering the colour of the double plate uniform, when it has ceased to be so by the action of the sugar.

Faraday made the remarkable discovery that, if a very strong electric current be passed round a substance which possesses the property of circular polarisation, the amount of rotation is altered to a considerable degree.

HEATING AND CHEMICAL RAYS OF THE SOLAR SPECTRUM.—The luminous rays of the sun are accompanied, as already mentioned, by others which possess heating powers. If the temperature of the different-coloured spaces in the spectrum be tried with a delicate thermometer, it will be found to increase from the violet to the red extremity, and when the prism is of some particular kinds of glass, the greatest effect will be manifested a little beyond the visible red rays. The position of the greatest heating effect in the spectrum materially depends on the absorptive nature of the glass. Transparent though this medium is to the rays of light, it nevertheless absorbs a considerable quantity of the heat rays. Transparent rock-salt is almost without absorptive action on the thermal rays. In the spectrum obtained by passing the solar rays through prisms of rock-salt, the greatest thermal effect is found at a position far beyond the last visible red rays. It is inferred from this that the chief mass of the heating rays of the sun are among the least refrangible components of the solar beam.

Again, it has long been known that chemical changes both of combination and of decomposition, but more particularly the latter, can be effected by the action of light. Chlorine and hydrogen combine at common temperatures only under the influence of light; and parallel cases occur in great numbers in organic chemistry. The blackening and decomposition of silver salts are familiar instances of the chemical powers of the same agent. Now, it is not always the luminous part of the ray which effects these changes; they are chiefly produced by certain invisible rays, which accompany the others, and are found most abundantly beyond the violet part of the spectrum. It is there that certain chemical effects are most marked, although the intensity of the light is exceedingly feeble. These chemically acting rays are sometimes called *actinic rays* (ἀκτίς, a ray), and the chemical action of sunlight is called *actinism*; but these terms are not very well chosen. The chemical rays are thus directly opposed to the heating rays in the common spectrum in their degree of refrangibility, since they exceed all the others in this respect. The luminous rays, too, under peculiar conditions, exert decomposing powers upon silver salts. The result of the action of any ray depends, moreover, greatly on the physical state of the surface uponwhich it falls, and on the chemical constitution of the body; indeed, for every kind of ray a substance may be found which under particular circumstances will be affected by it; and thus it appears that the chemical functions are by no means confined to any set of rays to the exclusion of the rest.

Upon the chemical changes produced by light is based the art of *photography*. In the year 1802 Mr Thomas Wedgwood proposed a method of copying paintings on glass, by placing behind them white paper or leather moistened with a solution of silver nitrate, which became decomposed and blackened by the transmitted light in proportion to the intensity of the latter; and Davy, in repeating these experiments, found that he could thus obtain tolerably accurate representations of objects of a texture partly opaque and partly transparent, such as leaves and the wings of insects, and even copy with a certain degree of success the images of small objects obtained by the solar microscope. These pictures, however, required to be kept in the dark, and could only be examined by candle-light, otherwise they became obliterated by the blackening of the whole surface, from which the salt of silver could not be removed. These attempts at light-painting attracted but little notice till the year 1839, when Mr Fox Talbot published his plan of "photogenic drawing." This consisted in exposing in the camera a paper soaked in a weak solution of common salt, and afterwards washed over with a strong solution of nitrate of silver; the image thus obtained was a *negative* one, the lights being dark and the shadows light, and the pictures were fixed by immersion in a solution of common salt.

Many improvements have been made in this process. In 1841 Fox Talbot patented the beautiful process known as the "Talbotype or Calotype process," in which the paper is coated with silver iodide by dipping it first in silver nitrate, then in potassium iodide.

Paper thus prepared is not sensitive *per se* to the action of light, but may be rendered so by washing it over with a mixture of silver nitrate and gallic or acetic acid. If it be exposed to the camera for two or three minutes, it does not receive a visible image (unless the light has been very strong); but still the compound has undergone a certain change by the influence of the light; for on subsequently washing it over with the mixture of silver nitrate and acetic or gallic acid, and gently warming it, a negative image comes out on it with great distinctness. This image is *fixed* by washing the paper with sodium hyposulphite, which removes the whole of the silver iodide not acted upon by the light, and thus protects the picture from further change by exposure to light. The negative picture thus obtained is rendered transparent by placing it between two sheets of blotting-paper saturated with white wax, and passing a moderately heated smoothing-iron over the whole. It may then be used for printing *positive pictures* by laying it on a sheet of paper prepared with chloride or iodide of silver and exposing it to the sun.

A most important step in the progress of photography is the substitution of a transparent film of iodised collodion or albumin spread upon glass, for the iodised paper used in Talbot's process, to receive the negative image in the camera. The process is thus rendered so much more certain and rapid, and the positive pictures obtained by transferring the negative to paper prepared with chloride or iodide of silver, are found to be so much sharper in outline than when the transference occurs through paper, as in the talbotype process, that this method is now universally employed. In this process, as in that of the Calotype, the image produced in the camera is a latent one, and requires development with substances such as pyrogallic acid, or ferrous sulphate, which, having a tendency to absorb oxygen, induce, in presence of silver nitrate, the reduction of the chloride or iodide to the metallic state. For a description of the best apparatus and latest processes used in the collodion method, the reader may consult Hardwich's "Manual of Photographic Chemistry."

Sir John Herschel has shown that a great number of other substances can be employed in these photographic processes by taking advantage of the deoxidising effects of certain portions of the solar rays. Paper washed with a solution of ferric salt becomes capable of receiving impressions of this kind, which may afterwards be made evident by potassium ferricyanide, or gold chloride. Vegetable colours are also acted upon in a very curious and apparently definite manner by the different parts of the spectrum.

The *daguerreotype*, the announcement of which was first made in the summer of 1839, by M. Daguerre, who had been occupied with this subject from 1826, if not earlier, is another remarkable instance of the decomposing effects of the solar rays. A clean and highly polished plate of silvered copper is exposed for a certain time to the vapour of iodine, and then transported to the camera obscura. In the most improved state of the process, a very short time suffices for effecting the necessary change in the film of silver iodide. The picture, however, becomes visible only by exposing it to the vapour of mercury, which attaches itself, in the form of exceedingly minute globules, to those parts which have been most acted upon, that is to say, to the lights, the shadows being formed by the dark polish of the metallic plate. Lastly, the plate is washed with sodium hyposulphite, to remove the undecomposed silver iodide and render it permanent.

Since Daguerre's time this process has undergone considerable improvements; amongst these, we may mention the exposure of the plate to the vapour of bromine, by which the sensitiveness of the film is greatly increased, and the reduction of metallic gold upon the surface of the film during the process of fixing, by which the lights and shades of the picture are rendered more effective.

Etching and lithographic processes, by combined chemical and photographic agency, promise to be of considerable utility. The earliest is that of Nièpce: he applied a bituminous coating to a metal plate, upon which an engraving was superimposed. The light, being thus partially interrupted, acted unequally upon the varnish; a liquid hydro-carbon, *petroleum*, used as a solvent, removed the bitumen wherever the light had not acted; an engraving acid could now bite the unprotected metal, which could eventually be printed from in the usual way. Very successful results have also been obtained by M. Fizeau, who submits the daguerreotype to the action of a mixture of dilute nitric acid, common salt, and potassium nitrate, when the silver only is attacked, the mercurialised portion of the image resisting the acid; an etching is thus obtained following minutely the lights and shadows of the picture. To deepen this etching, the silver chloride formed is removed by ammonia, the plate is boiled in caustic potash and again treated with acid, and so on till the etching is of sufficient depth. Sometimes electro-gilding is resorted to, and an engraving acid is used to get still more powerful impressions.

Among recent results are those obtained by Mr Talbot on steel plates: he uses a mixture of potassium bichromate and gelatin, which hardens by exposure to the light; the parts not affected are removed by washing. Platinum tetrachloride is used as an etching liquid: it has the advantage of biting with greater regularity than nitric acid.

The bitumen process of M. Nièpce has been applied to lithographic stone; and positives obtained from negative talbotypes have been printed off by a modification of the ordinary lithographic process. M. Nièpce finds that ether dissolves the altered bitumen, while naphtha, or benzol, attacks by preference the bitumen in its normal condition.

MAGNETISM.

A PARTICULAR species of iron ore has long been remarkable for its property of attracting small pieces of iron, and causing them to adhere to its surface; it is called loadstone, or magnetic iron ore.

If a piece of this loadstone be carefully examined, it will be found that the attractive force for particles of iron is greatest at certain particular points of its surface, while elsewhere it is much diminished, or even altogether absent. These attractive points are denominated poles, and the loadstone itself is said to be endowed with magnetic polarity.

If one of the pole-surfaces of a natural loadstone be rubbed in a particular manner over a bar of steel, its characteristic properties will be communicated to the bar, which will then be found to attract iron-filings like the loadstone itself. Further, the attractive force will appear to be greatest at two points situated very near the extremities of the bar, and least of all towards the middle. The bar of steel so treated is said to be magnetised, or to constitute an artificial magnet.

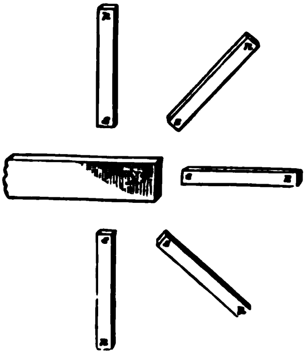
When a magnetised bar or natural magnet is suspended at its centre in any convenient manner, so as to be free to move in a horizontal plane, it is always found to assume a particular direction with regard to the earth, one end pointing nearly north, and the other nearly south. This direction varies with the geographical position of the place, and is different also at the same place at different times. In London, at the present time, the needle points 19° 32′ west of the astronomical north. If the bar be moved from this position, it will tend to reassume it, and, after a few oscillations, settle at rest as before. The pole which points towards the astronomical north is usually distinguished as the north pole of the bar, and that which points southward as the south pole.

A magnet, either natural or artificial, of symmetrical form, suspended in the presence of a second magnet, serves to exhibit certain phenomena of attraction and repulsion which deserve particular attention. When a north pole is presented to a south pole, or a south pole to a north, attraction ensues between them; the ends of the bars approach each other, and, if permitted, adhere with considerable force; when, on the other hand, a north pole is brought near a second north pole, or a south pole near another south pole, mutual repulsion is observed, and the ends of the bars recede from each other as far as possible. *Poles of an opposite name attract, and poles of a similar name repel each other.* Thus, a small bar or needle of steel, properly magnetised and suspended, and having its poles marked, becomes an instrument fitted not only to discover the existence of magnetic power in other bodies, but to estimate the kind of polarity affected by their different parts.

A piece of soft iron brought into the neighbourhood of a magnet acquires itself magnetic properties: the intensity of the power thus conferred depends upon that of the magnet, and upon the space which divides the two, becoming greater as that space decreases, and greatest of all in actual contact. The iron, under these circumstances, is said to be magnetised by *induction* or influence, and the effect, which reaches its maximum in an instant, is at once destroyed by removing the magnet.

When steel is substituted for iron in this experiment, the inductive action is hardly perceptible at first, and becomes manifest only after the lapse of a certain time: in this condition, when the steel bar is removed from the magnet, it retains a portion of the induced polarity. It becomes, indeed, a permanent magnet, similar to the first, and retains its peculiar properties for an indefinite time. This resistance which steel always offers in a greater or less degree both to the development of magnetism and to its subsequent destruction, is called *specific coercive power*.

Fig. 50.



The rule which regulates the induction of magnetic polarity in all cases is exceedingly simple, and most important to be remembered. The pole produced is always of the opposite name to that which produced it, a north pole developing south polarity, and a south pole north polarity. The north pole of the magnet figured in the sketch induces south polarity in all the nearer extremities of the pieces of iron or steel which surround it, and a state similar to its own in all the more remote extremities. The iron thus magnetised is capable of exerting a similar inductive action on a second piece, and that upon a third, and so to a great number, the intensity of the force diminishing as the distance from the permanent magnet increases. It is in this way that a magnet is enabled to hold up a number of small pieces of iron, or a bunch of filings, each separate piece becoming for the time a magnet by induction.

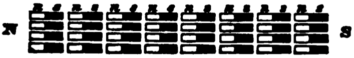
Magnetic polarity, similar in degree to that which iron presents, has been found only in some of the compounds of iron, in nickel, and in cobalt.

Magnetic attractions and repulsions are not in the slightest degree interfered with by the interposition of substances destitute of magnetic properties. Thick plates of glass, shellac, metals, wood, or of any substances except those above mentioned, may be placed between a magnet and a suspended needle, or a piece of iron under its influence, the distance being preserved, without the least perceptible alteration in its attractive power, or force of induction.

One kind of polarity cannot be exhibited without the other. In other words, a magnetic pole cannot be isolated. If a magnetised bar of steel be broken at its neutral point, or in the middle, each of the broken ends acquires an opposite pole, so that both portions of the bar become perfect magnets; and, if the division be carried still further, if the bar be broken into a hundred pieces, each fragment will be a complete magnet, having its own north and south poles.

This experiment serves to show very clearly that the apparent polarity of the bar is the consequence of the polarity of each individual particle, the poles of the bar being merely points through which the resultants of all these forces pass; the largest magnet is made up of an immense number of little magnets regularly arranged side by side, all having their north poles looking one way, and their south poles the other. The middle portion of such a system cannot possibly exhibit attractive or repulsive effects on an external body, because each pole is in close juxtaposition with one of an opposite name and of equal power. Hence their forces will be exerted in opposite directions, and neutralise each other's influence. Such will not be the case at the extremities of the bar; there uncompensated polarity will be found, capable of exerting its specific power.

Fig. 51.



This idea of regular polarisation of particles of matter in virtue of a pair of opposite and equal forces, is not confined to magnetic phenomena; it is the leading principle in electrical science, and is constantly reproduced in some form or other in every discussion involving the consideration of molecular forces.

Artificial steel magnets are made in a great variety of forms; such as small light needles, mounted with an agate cap for suspension upon a fine point; straight bars of various kinds; bars curved into the shape of a horse-shoe, &c. All these have regular polarity communicated to them by certain processes of rubbing or touching with another magnet, which require care, but are not otherwise difficult of execution. When great power is wished for, a number of bars may be screwed together, with their similar ends in contact, and in this way it is easy to construct permanent steel magnets capable of sustaining great weights. To prevent the gradual destruction of magnetic force, which would otherwise occur, it is usual to arm each pole with a piece of soft iron or keeper, which, becoming magnetised by induction, serves to sustain the polarity of the bar, and in some cases even increases its energy.

Magnetism is not peculiar to these substances which have more especially been called magnetic, such as iron, nickel, cobalt, but it is the property of all metals, though to a much smaller degree. Very powerful magnets are required to show this remarkable fact. Large horse-shoe magnets, made by the action of the electric current, are best adapted for the purpose. The magnetic action on different substances which are capable of being easily moved, differs not only according to the size, but also according to the nature of the substance. In consequence of this, Faraday divides all bodies into two classes. He calls the one magnetic, or, better, *paramagnetic*, and the other *diamagnetic*.

The matter of which a paramagnetic (magnetic) body consists is attracted by both poles of the horse-shoe magnet; on the contrary, the matter of a diamagnetic body is repelled. When a small iron bar is hung by untwisted silk between the poles of the magnet, so that its long diameter can easily move in a horizontal plane, it arranges itself axially, that is, parallel to the straight line which joins the poles, or to the magnetic axis of the poles, assuming at the end which is nearest the north pole, a south pole, and at the end nearest the south pole, a north pole. Whenever the little bar is removed from this position, it returns, after a few oscillations, to its previous position. The whole class of paramagnetic bodies behave in a precisely similar way under similar circumstances, but in the intensity of the effects great differences occur.

Diamagnetic bodies, on the contrary, have their long diameters placed equatorially, that is, at right angles to the magnetic axis. They behave as if at the end opposite to each pole of the magnet the same kind of polarity existed.

In the first class of substances, besides iron, which is the best representative of the class, we have nickel, cobalt, manganese, chromium, cerium, titanium, palladium, platinum, osmium, aluminium, oxygen, and also most of the compounds of these bodies, most of them, even when in solution. According to Faraday, the following substances are also feebly paramagnetic (magnetic),—paper, sealing-wax, Indian-ink, procelain, asbestos, fluor-spar, minium, cinnabar, binoxide of lead, sulphate of zinc, tourmaline, graphite, and charcoal.

In the second class are placed bismuth, antimony, zinc, tin, cadmium, sodium, mercury, lead, silver, copper, gold, arsenic, uranium, rhodium, iridium, tungsten, phosphorus, iodine, sulphur, chlorine, hydrogen, and many of their compounds. Also, glass free from iron, water, alcohol, ether, nitric acid, hydrochloric acid, resin, wax, olive oil, oil of turpentine, caoutchouc, sugar, starch, gum, and wood. These are diamagnetic.

When diamagnetic and paramagnetic bodies are combined, their peculiar properties are more or less neutralised. In most of these compounds, occasionally in consequence of the presence of a very small quantity of iron, the peculiar magnetic power remains more or less in excess. Thus green bottle-glass, and many varieties of crown glass, are magnetic in consequence of the iron they contain.

In order to examine the magnetic properties of liquids, they are placed in very thin glass tubes, the ends of which are then closed by melting; they are then hung horizontally between the poles of the magnet. Under the influence of poles sufficiently powerful, they begin to swing, and according as the fluid contents are paramagnetic (magnetic) or diamagnetic, they assume an axial or equatorial position.

Faraday has tried the magnetic condition of gases in different ways. One method consisted in making soap-bubbles with the gas which he wished to investigate, and bringing these near the poles. Soap and water alone is feebly diamagnetic. A bubble filled with oxygen was strongly attracted by the magnet. All other gases in the air are diamagnetic, that is, they are repelled. But, as Faraday has shown, in a different way, this partly arises from the paramagnetic (magnetic) property of the air. Thus he found that nitrogen, when this differential action was eliminated, was perfectly indifferent, whether it was condensed or rarefied, whether cooled or heated. When the temperature is raised, the diamagnetic property of gases in the air is increased. Hence the flame of a candle or of hydrogen is strongly repelled by the magnet. Even warm air is diamagnetic in cold air.

For some time it had been believed that crystallised bodies exhibited a special and peculiar behaviour when placed between the poles of a magnet. It appeared as though the magnetic directing power of the crystal had some peculiar relation to the position of its optic axis; so that, independently of the magnetic property of the substance of the crystal, if the crystal were positively optical, it possessed the power of placing its optic axis parallel with the line which joined the poles of the magnet, while optically negative crystals tried to arrange their axis at right angles to this line. This supposition is disproved by the excellent investigation of Tyndall and Knoblauch, who showed that exceptions to the above law are furnished by all classes of crystals, and proved that the action, instead of being independent of the magnetic nature of the mass, was completely reversed where, in isomorphous crystals, a magnetic constituent was substituted for a diamagnetic one. Rejecting the various new forces assumed, Tyndall and Knoblauch referred the observed phenomena to the modification of the magnetic force by structure, and they imitated the effects exactly by means of substances whose structure had been modified by compression. In a later investigation Tyndall demonstrated the fundamental principle on which these phenomena depend, showing that the *entire mass* of a magnetic body is most strongly attracted when the attracting force acts parallel to the line of compression; and that a diamagnetic substance is most strongly repelled when the repulsion acts along the same line. Hence when such a body is freely suspended in the magnetic field, the line of compression must set axially or equatorially, according as the mass is magnetic or diamagnetic. Faraday was the first to establish a differential action of this kind in the case of bismuth; Tyndall extended it to several magnetic and diamagnetic crystals, and showed that it was not confined to them, but was a general property of matter. It was also proved that for a fixed distance the attraction of a magnetic sphere, and the repulsion of a diamagnetic sphere, followed precisely the same law, both being exactly proportioned to the square of the exciting current.

The phenomena of diamagnetism naturally suggest the inquiry, whether the repulsion exerted by a magnetic pole on diamagnetic bodies is a force distinct from that of magnetism as exerted upon iron and other bodies of the magnetic class; or whether, on the other hand, the magnetic and diamagnetic conditions of matter are merely relative, so that all bodies are magnetic in different degrees, and the apparent repulsion of a diamagnetic body, such as bismuth, is merely the result of its being attracted by the magnet less than the particles of the surrounding medium, just as a balloon recedes from the earth because its weight is less than that of an equal bulk of the surrounding air. It is easy to show that the same body may appear magnetic or diamagnetic, according to the medium in which it is placed. Ferrous sulphate is a magnetic substance, and water is diamagnetic: hence it is possible, by varying the strength of an aqueous solution of this salt, to make it either magnetic, indifferent, or diamagnetic, when suspended in air. Again, a tube containing a solution of ferrous sulphate suspended horizontally within a jar also filled with a solution of the same salt, and placed between the poles of two powerful electromagnets, will place itself axially or equatorially, according as the solution contained in it is stronger or weaker than that in the jar. In the same manner, then, we may conceive that bismuth places itself equatorially between two magnetic poles, because it is less magnetic than the surrounding air. But the diamagnetism of bismuth and other bodies of the same class shows itself in a vacuum as well as in air: hence, if diamagnetism is not to be regarded as a distinct force, we must suppose that the *ether* is also magnetic, and occupies in the magnetic scale the place intermediate between magnetic and diamagnetic bodies.

That a body suspended in a medium of greater magnetic susceptibility than itself will recede from a magnetic pole in its neighbourhood, in consequence of the greater force with which the particles of the medium are impelled towards the magnet, is so obvious a consequence of mechanical laws, that we can scarcely avoid attributing the movements of diamagnetic bodies to the cause just mentioned; at least, when the body is suspended in air or other magnetic gas. There is, however, some difficulty in reconciling the above-described phenomena of compressed and crystallised bodies with this view; and, moreover, Tyndall has shown, by a method which we cannot here describe,* that diamagnetic bodies possess opposite poles, analogous to those of magnetic bodies, each of these poles being attracted by one pole of a magnet, and repelled by the other. This polarity shows decidedly that the properties of diamagnetic bodies cannot be wholly due to the differential action above mentioned; for if they were, every part of a diamagnetic body would be repelled by either pole of a magnet. Diamagnetism must therefore, for the present at least, be regarded as a force distinct from magnetism.

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* Phil. Trans., 1855 and 1856; see also Watts's Dictionary of Chemistry, vol. iii. p. 776.

ELECTRICITY.

When glass, amber, or sealing-wax is rubbed with a dry cloth, it acquires the power of attracting light bodies, as feathers, dust, or bits of paper; this is the result of a new and peculiar condition of the body rubbed, called electrical excitation.

If a light downy feather be suspended by a thread of white silk, and a dry glass tube, excited by rubbing, be presented to it, the feather will be strongly attracted to the tube, adhere to its surface for a few seconds, and then fall off. If the tube be now excited anew, and presented to the feather, the latter will be strongly repelled.

The same experiment may be repeated with shellac or resin; the feather in its ordinary state will be drawn towards the excited body, and, after touching, again driven from it with a certain degree of force.

Now, let the feather be brought into contact with the excited glass, so as to be repelled by that substance, and let a piece of excited sealing-wax be presented to it: a degree of attraction will be observed far exceeding that exhibited when the feather is in its ordinary state. Or, again, let the feather be made repulsive for sealing-wax, and then the excited glass be presented: strong attraction will ensue.

The reader will at once see the perfect parallelism between the effects described and some of the phenomena of magnetism, the electrical excitement having a twofold nature, like the opposite polarities of the magnet. A body to which one kind of excitement has been communicated is attracted by another body in the opposite state, and repelled by one in the same state; the excited glass and resin being to each other as the north and south poles of a pair of magnetised bars.

To distinguish these two different forms of excitement, terms are employed which, although originating in some measure in theoretical views of the nature of the electrical disturbance, may be understood by the student as purely arbitrary and distinctive: it is customary to call the electricity manifested by glass rubbed with silk *positive* or *vitreous*, and that developed in the case of shellac, and bodies of the same class rubbed with flannel, *negative* or *resinous*. The kind of electricity depends in some measure upon the nature of the surface and the quality of the rubber; smooth and perfectly clean glass, rubbed with silk, becomes positive, but when ground or roughened by sand or emery, it acquires, under the same circumstances, a negative charge. Glass dried over a gas flame and rubbed with wool is generally also negative; when dried over a fire of wood-charcoal it remains positive.

The repulsion shown by bodies in the same electrical state is taken advantage of to construct instruments for indicating electrical excitement and pointing out its kind. Two balls of elder pith, hung by threads or very fine metal wires, serve this purpose in many cases: they open out when excited, in virtue of their mutual repulsion, and show by the degrees of divergence the extent to which the excitement has been carried. A pair of gold leaves suspended to a metal rod having a brass plate on its upper end constitute a much more delicate arrangement, and one of great value in all electrical investigations. The rod should be covered with a thick coating of shellac, and it must be fastened by means of a cork, air-tight, into a glass flask. The flask must have been perfectly dried previously by warming it. These instruments are called electroscopes or electrometers: when excited by the communication of a known kind of electricity, they show, by an increased or diminished divergence, the state of an electrified body brought into their neighbourhood (fig. 53).

Fig. 52.

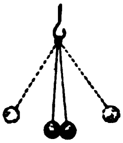
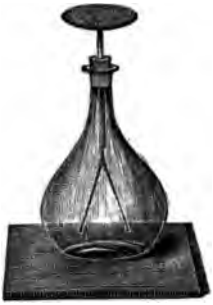
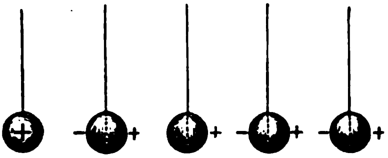


Fig. 53.



One kind of electricity can no more be developed without the other than one kind of magnetism: the rubber and the body rubbed always assume opposite states, and the positive condition on the surface of a mass of matter is invariably accompanied by a negative state in all surrounding bodies.

Fig. 54.



The induction of magnetism in soft iron has its exact counterpart in electricity: a body already electrified disturbs or polarises the particles of all surrounding substances in the same manner and according to the same law, inducing a state opposite to its own in the nearer portions, and a similar state in the more remote parts A series of globes suspended by silk threads, in the manner represented in fig. 54, will each become electric by induction when a charged body is brought near the end of the series, like so many pieces of iron in the vicinity of a magnet, the positive half of each globe looking in one and the same direction, and the negative half in the opposite one. The positive and negative signs are intended to represent the opposite states.

The intensity of the induced electrical disturbance diminishes with the distance from the charged body; if this be removed or discharged, all the effects cease at once.

So far, the greatest resemblance may be traced between these two sets of phenomena; but here it seems in great measure to cease. The magnetic polarity of a piece of steel can awaken polarity in a second piece in contact with it by the act of induction, and in so doing loses nothing whatever of its power: this is an effect completely different from the apparent transfer or discharge of electricity constantly witnessed, which in the air and in liquids often gives rise to the appearance of a bright spark of fire. Indeed ordinary magnetic effects comprise two groups of phenomena only, those, namely, of attraction and repulsion, and those of induction. But in electricity, in addition to phenomena very closely resembling these, we have the effects of *discharge*, to which there is nothing analogous in magnetism, and which takes place in an instant when any electrified body is put in communication with the earth by any one of the class of substances called conductors of electricity, all signs of electrical disturbance then ceasing.

These conductors of electricity, which thus permit discharge to take place through their mass, are contrasted with another class of substances called non-conductors or insulators. The difference, however, is only one of degree, not of kind; the very best conductors offer a certain resistance to the electrical discharge, and the most perfect insulators permit it to a small extent. The metals are by far the best conductors; glass, silk, shellac, and dry gas, or vapour of any sort, the very worst; and between these there are bodies of all degrees of conducting power.

In good conductors of sufficient size electrical discharges take place silently and without disturbance. But if the charge be very intense, and the conductor very small, or imperfect from its nature, it is often destroyed with violence.

When a break is made in a conductor employed in effecting the discharge of a highly excited body, disruptive or spark-discharge takes place across the intervening air, provided the ends of the conductor be not too distant. The electrical spark itself presents many points of interest in the modifications to which it is liable.

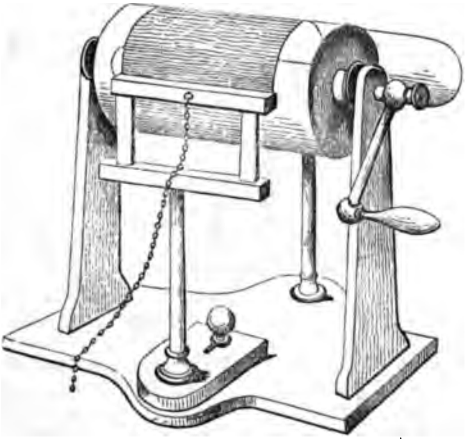
The time of transit of the electrical wave through a chain of good conducting bodies of great length is so minute as to be altogether inappreciable to ordinary means of observation. Professor

Wheatstone's very ingenious experiments on the subject give, in the instance of motion through a copper wire, a velocity surpassing that of light.

Electrical excitation is manifested only upon the surfaces of conductors, or those portions directed towards other objects capable of assuming the opposite state. An insulated ball charged with positive electricity, and placed in the centre of the room, is maintained in that state by the inductive action of the walls of the apartment, which immediately become negatively electrified; in the interior of the ball there is absolutely no electricity to be found, although it may be constructed of open metal gauze, with meshes half an inch wide. Even on the surface the distribution of electrical force is not always the same; it depends upon the figure of the body itself, and its position with regard to surrounding objects. The polarity is always highest in the projecting extremities of the same conducting mass, and greatest of all when these are attenuated to points; in which case the inequality becomes so great that discharge takes place to the air, and the excited condition cannot be maintained.

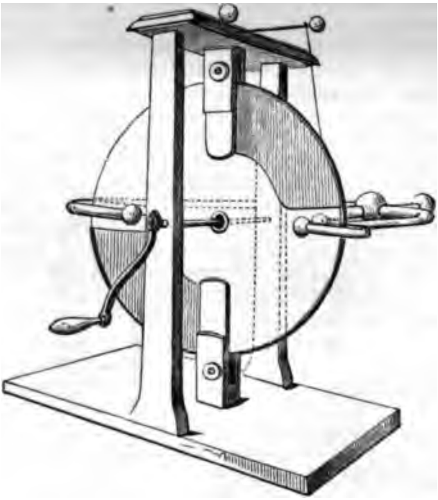
By the aid of these principles, the construction and use of the common electrical machine, and other pieces of apparatus of great utility, will become intelligible.

Fig. 55.



A glass cylinder (fig. 55) is mounted with its axis in a horizontal position, and provided with a handle or winch by which it may be turned. A leather cushion is made to press by a spring against one side of the cylinder, while a large metal conducting body, armed with a number of points next the glass, occupies the other: both cushion and conductor are insulated by glass supports, and to the upper edge of the former a piece of silk is attached long enough to reach half round the cylinder. Upon the cushion is spread a quantity of soft amalgam of tin, zinc, and mercury,* mixed up with a little grease: this substance is found by experience to excite glass most powerfully. The cylinder, as it turns, becomes charged by friction against the rubber, and as quickly discharged by the row of points attached to the great conductor; and as the latter is also completely insulated, its surface speedily acquires a charge of positive electricity, which may be communicated by contact to other insulated bodies. The maximum effect is produced when the rubber is connected by a chain or wire with the earth. If negative electricity be wanted, the rubber must be insulated and the conductor discharged.

Fig. 56.



Another form of the electrical machine consists of a circular plate of glass (fig. 56) moving upon an axis, and provided with two pairs of cushions or rubbers, attached to the upper and lower parts of the wooden frame, covered with amalgam, between which the plate moves with considerable friction. An insulated conductor, armed as before with points, discharges the plate as it turns, the rubber being at the same time connected with the ground by the wood-work of the machine, or by a strip of metal. This form of the apparatus is preferred in all cases where considerable power is wanted.

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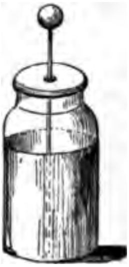
* 1 part tin, 1 zinc, and 6 mercury. An amalgam of permanent softness and great efficacy is obtained by mixing 65 parts mercury, 24 tin, and 11 zinc. It is better applied to silk than to leather.

In the management of electrical apparatus, great care must be taken to prevent deposition of moisture from the air upon the surface of the glass supports, which should always be varnished with fine lac dissolved in alcohol; the slightest film of water is sufficient to destroy the power of insulation. The rubbers also must be carefully dried, and, like the plate, cleansed from adhering dust before use, and the amalgam renewed if needful: in damp weather much trouble is often experienced in bringing the machine into powerful action.

When the conductor of the machine is charged with electricity, it acts indirectly on, and accumulates the contrary electricity to its own, at the surface of all the surrounding conductors. It produces the greatest effect on the conductor that is nearest to it and is in the best connection with the ground, whereby the electricity of the same kind as that of the machine may pass to the earth. As the inducing electricity attracts the induced electricity of an opposite kind, so, on the other hand, is the former attracted by the latter. Hence, the electricity which the conductor receives from the machine must especially accumulate at that spot to which another good conductor of electricity is opposed. If a metal disc is in connection with the conductor of a machine, and if another similar disc, in good connection with the earth, is placed opposite to to it, we have an arrangement by which tolerably large and good conducting surfaces can be brought close to one another: thus the positive condition of the first disc, as well as the negative condition of the other, must be increased to a very considerable degree: the limit is in this case, however, soon reached, because the intervening air easily permits spark-discharge to take place through its substance. With a solid insulating body, as glass or lac, this happens with much greater difficulty, even when the plate of insulating matter is very thin. It is on this principle that instruments for the *accumulation* of electricity depend, among which the Leyden jar is the most important.

Fig. 57.



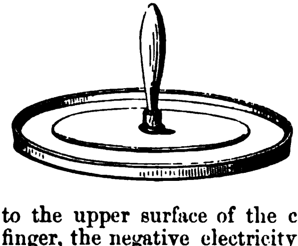
A thin glass jar is coated on both sides with tinfoil, care being taken to leave several inches of the upper part uncovered (fig. 57); a wire, terminating in a metallic knob, communicates with the internal coating. When the outside of the jar is connected with the earth, and the knob put in contact with the conductor of the machine, the inner and outer surfaces of the glass become respectively positive and negative, until a very great degree of intensity has been attained. On completing the connection between the two coatings by a metallic wire or rod, discharge occurs in the form of an exceedingly bright spark, accompanied by a loud snap: and if the human body be interposed in the circuit, the peculiar and disagreeable sensation of the electric shock is felt at the moment of its completion.

By enlarging the dimensions of the jar, or by connecting together a number of such jars in such a manner that all may be charged and discharged simultaneously, the power of the apparatus may be greatly augmented. Thin wires of metal may be fused and dissipated; pieces of wood may be shattered; many combustible substances set on fire; and all the well-known effects of lightning exhibited upon a small scale.

The electric spark is often very conveniently employed in chemical inquiries for firing gaseous mixtures in closed vessels. A small Leyden jar charged by the machine is the most effective contrivance for this purpose; but, not unfrequently, a method may be resorted to which involves less preparation. This method was devised by Bunsen. A large porcelain tube, which is dry and warm, is wrapped round and rubbed briskly by a dry silken cloth, and after each rub, the tube is brought in the immediate neighbourhood of the knob of a small Leyden jar, the outer coating of this vessel being in connection with the earth.

The electrophorus (fig. 58) is also frequently used for this purpose. This instrument consists of a round tray or dish of tinned plate, having a stout wire round its upper edge; the width may be about twelve inches, and the depth half an inch. This tray is filled with melted shellac, and the surface rendered as even as possible. A brass disc, with rounded edge, of about nine inches diameter, is also provided, and fitted with an insulating handle. The resinous plate is excited by striking it with a dry, warm piece of fur or flannel, whereby it becomes charged with negative electricity. If the cover be then placed upon it, the positive electricity is drawn to the under surface of the metal nearest to the negatively charged resinous cake, while the negative electricity is repelled to the upper surface of the cover; on touching the cover with the finger, the negative electricity passes away to the earth, while an additional quantity of positive electricity is drawn into the plate; and if the finger be removed and the cover then lifted by its insulating handle, it will be found so strongly charged by induction with positive electricity as to give a bright spark; and as the resin is not discharged by the cover, which merely touches it at a few points, sparks may be drawn as often as may be wished.

Fig. 58.



Atmospheric Electricity.—It is not known to what cause the disturbance of the electrical equilibrium of the atmosphere is due: experiment has shown that the higher regions of the air are usually in a positive state, the intensity of which reaches a maximum at a particular period of the day. In cloudy and stormy weather the distribution of the atmospheric electricity becomes much deranged, clouds near the surface of the earth often appearing in a negative state.

The circumstances of a thunderstorm exactly resemble those of the charge and discharge of a coated plate or jar; the cloud and the earth represent the two coatings, and the intervening air the bad conducting body, or *dielectric.* The polarities of the opposed surface and of the insulating medium between them become raised by mutual induction, until violent disruptive discharge takes place through the air itself, or through any other bodies which may happen to be in the interval. When these are capable of conducting freely, the discharge is silent and harmless; but in other cases it often proves highly destructive. These dangerous effects are now in a great measure obviated by the use of lightning-rods attached to buildings, the erection of which, however, demands a number of precautions not always understood or attended to. The masts of ships may be guarded in like manner by metal conductors. Sir W. Snow Harris has devised a most ingenious plan for the purpose, which is now adopted, with complete success, in the Royal Navy.

The electricity exhibited under certain circumstances by a jet of steam, first observed by mere accident, but since closely investigated by Sir W. Armstrong, and afterwards by Faraday, is now referred to the friction, not of the pure steam itself, but of particles of condensed water, against the interior of the exit-tube. It has been proved with certainty in the last few years that evaporation alone is not capable of disturbing the electrical equilibrium, and the hope first entertained, that these phenomena would throw light upon the cause of electrical excitement in the atmosphere, is now abandoned. The steam is usually positive if the jet-pipe be constructed of wood or clean metal, but the introduction of the smallest trace of oily matter causes a change of sign. The intensity of the charge is, *cæteris paribus*, increased with the elastic force of the steam. By this means effects have been obtained very far surpassing those of the most powerful plate electrical machines ever constructed.

Although no electricity can be directly evolved by evaporation, yet vapour possesses in a high degree the property of discharging into the atmosphere that electricity which often accumulates in bodies from which it arises. The fresh branches and leaves of trees do this to the greatest extent. When moistened with rain or dew, their surfaces become positively electrical, whilst the internal parts, even to the roots, become negatively electrical.

ELECTRIC CURRENT; ELECTRIC BATTERY.

When two solid conducting bodies are plunged into a liquid **which acts upon** them unequally, the electric equilibrium is disturbed, the one acquiring the positive condition, and the other the negative. Thus, pieces of zinc and platinum put into dilute sulphuric acid, constitute an arrangement capable of generating electrical force: the zinc which is the metal attacked, becomes negative; the platinum which remains unaltered, assumes the positive condition; and on making a metallic communication in any way between the two plates, discharge ensues, as when the two surfaces of a coated and charged jar are put into connection.

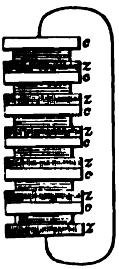
No sooner, however, has this occurred, than the disturbance is repeated; and as these successive charges and discharges take place through the fluid and metals with inconceivable rapidity, the result is an apparently continuous action, to which the term *electrical current* is given.

It is necessary to guard against the idea, which the term naturally suggests, of an actual bodily transfer of something through the substance of the conductors, like water through a pipe: the real nature of all these phenomena is entirely unknown; the expression is convenient notwithstanding, and consecrated by long use; and with this caution, the very dangerous error of applying figurative language to describe an effect, and then seeking the nature of the effect from the common meaning of words, may be avoided.

The intensity of the electrical excitement developed by a single pair of metals and a liquid is too feeble to affect the most delicate gold-leaf electroscope; but, by arranging a number of such alternations in a connected series, in such a manner that the direction of the current shall be the same in each, the intensity may be very greatly exalted. The two instruments, invented by Volta, called the pile and crown of cups, depend upon this principle.

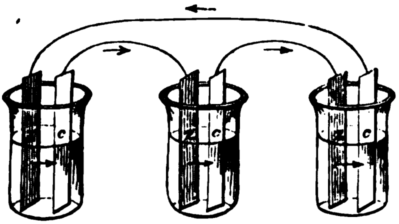
Upon a plate of zinc is laid a piece of cloth, rather smaller than itself, steeped in dilute acid, or any liquid capable of exerting chemical action upon the zinc; upon this is placed a plate of copper, silver, or platinum; then a second piece of zinc, another cloth, and a plate of inactive metal, until a pile of about twenty alternations has been built up. If the two terminal plates be now touched with wet hands, the sensation of the electrical shock will be experienced; but, unlike the momentary effect produced by the discharge of a jar, the sensation can be repeated at will by repeating the contact, and with a pile of one hundred such pairs, excited by dilute acid, it will be nearly insupportable. When such a pile is insulated, the two extremities exhibit strong positive and negative states; and when connection is made between them by wires armed with points of hard charcoal or plumbago, the discharge takes place in the form of a bright enduring spark or stream of fire.

Fig. 59.



The second form of apparatus, or crown of cups, is precisely the same in principle, although different in appearance. A number of cups or glasses are arranged in a row or circle, each containing a piece of active and a piece of inactive metal, and a portion of exciting liquid—zinc, copper, and dilute sulphuric acid, for example. The copper of the first cup is connected with the zinc of the second, the copper of the second with the zinc of the third, and so to the end of the series. On establishing a communication between the first and last plates by means of a wire, or otherwise, discharge takes place as before.

Fig. 60.

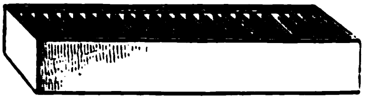


When any such electrical arrangement consists merely of a single pair of conductors and an interposed liquid, it is called a "simple circuit;" when two or more alternations are concerned, the term "compound circuit" is applied: they are called also, indifferently, Voltaic batteries. In every form of such apparatus, however complex it may appear, the direction of the current may be easily understood and remembered

When both ends of the series are insulated, the zinc end exhibits negative, the copper or platinum end positive electricity; consequently, when the two extremities or poles are joined by a conducting wire and a complete circuit formed, the current of positive electricity proceeds *without* the battery from the platinum or copper to the zinc, and *within* the battery, from the zinc to the copper or platinum, as indicated by the arrows—just as in the common electrical machine, when the positive conductor and the rubber are joined by a wire, the positive current proceeds from the conductor through the wire to the rubber, and thence along the surface of the glass cylinder or plate to the conductor again.

In the modification of Volta's original pile, made by Cruikshank, the zinc and copper plates are soldered together, and

Fig. 61.

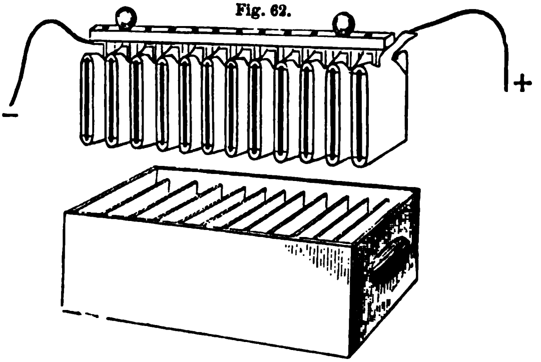


cemented water-tight into a mahogany trough, which thus becomes divided into a series of cells or compartments capable of receiving the exciting liquid. This apparatus (fig. 61) is well fitted to exhibit effects of *tension*, to act upon the electroscope, and give shocks: hence its advantageous employment in the application of electricity to medicine.

A form of battery more convenient for most purposes is that contrived by Wollaston (fig. 62). In this the copper is made completely to encircle the zinc plate, except at the edges, the two metals being kept apart by pieces of cork or wood. Each zinc is soldered to the preceding copper, and the whole screwed to a bar of dry mahogany, so that the plates can be lifted into or out of the acid, which is contained in an earthenware trough, divided into separate cells. The liquid consists of a mixture of 100 parts water, 2¼ parts oil of vitriol, and two parts commercial nitric acid, all by measure. A number of such batteries are easily connected together by straps of sheet copper, and admit of being put into action with great ease.

In all these older forms of the voltaic battery, however, the power rapidly decreases, so that, after a short time, scarcely the tenth part of the original action remains. This loss of power depends partly on the gradual change of the sulphuric acid into zinc sulphate, but still more on other causes, which, together with the more modern forms of the battery which have been contrived to obviate them, will be more easily understood at a subsequent part of the work, when we come to consider the nature and effects of electro-chemical decomposition.

Fig. 62.



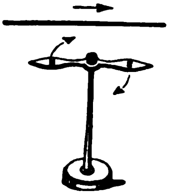
The term "galvanism," sometimes applied to this branch of electrical science, is used in honour of Galvani, of Bologna, who, in 1790, made the very curious observation that convulsions could be produced in the limbs of a dead frog when certain metals were made to touch the nerve and muscle at the same moment. It was Volta, however, who pointed out the electrical origin of these motions; and although the explanation he offered of the source of the electrical disturbance is no longer generally adopted, his name is very properly associated with the invaluable instrument his genius gave to science.

ELECTRO-MAGNETISM.

Although the fact that electricity is capable, under certain circumstances, both of inducing and of destroying magnetism, has long been known from the effects of lightning on the compass-needle and upon small steel articles, as knives and forks, to which polarity has suddenly been given by the stroke, it was not until 1819 that the laws of these phenomena were discovered by Oersted, of Copenhagen, and shortly afterwards fully developed by Ampère.

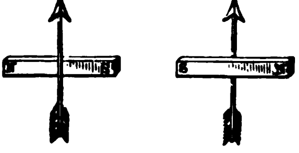
If a wire conveying an electrical current be brought near a magnetic needle, the latter will immediately alter its position, and assume a new one as nearly perpendicular to the wire as the mode of suspension and the magnetism of the earth will permit. When the wire, for example, is placed directly over the needle, and parallel to its length, while the current it carries travels from north to south, the needle is deflected from its ordinary direction, and the north pole driven to the eastward. When the current is reversed, the same pole deviates to an equal amount towards the west. Placing the wire below the needle instead of above produces the same effect as reversing the current.

Fig. 63.



The direction which the needle will assume when placed in any particular position to the conducting wire may be determined by the following rule:—*Let the current be supposed to pass through a watch from the face to the back: the motion of the north pole will be in the direction of the hands.* Or, *let the observer imagine himself swimming in the direction of the current with his face towards the needle: the north pole of the needle will then be deflected towards his left hand.*

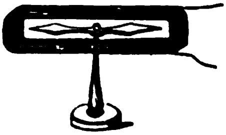
Fig. 64.



If reference is often required, a little piece of apparatus (fig. 64) may be used, consisting of a piece of pasteboard, or other suitable material, cut into the form of an arrow for indicating the current, crossed by a magnet having its poles marked, and arranged in the true position with respect to the current. The direction of the latter in the wire of the galvanoscope can at once be known by placing the representative magnet in the direction assumed by the needle itself.

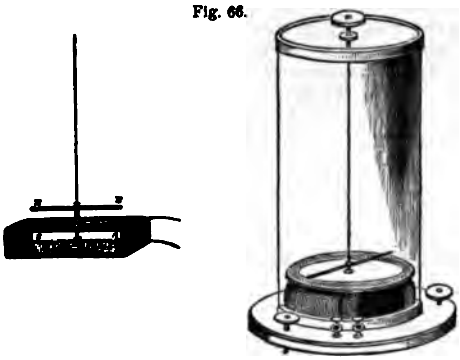
When the needle is subjected to the action of two currents in opposite directions, the one above and the other below, they will obviously concur in their effects. The same thing happens when the wire carrying the current is bent upon itself, and the needle placed between the two portions as in fig. 65; and since every time the bending is repeated, a fresh portion of the current is made to act in the same manner upon the needle, it is easy to see how a current, too feeble to produce any effect when a simple straight wire is employed, may be made by this contrivance to exhibit a powerful action on the magnet. It is on this principle that instruments called *galvanometers*, *galvanoscopes*, or *multipliers*, are constructed; they serve not only to indicate the existence of electrical currents, but to show, by the effects upon the needle, the direction in which they are moving.

Fig. 65.



The delicacy of the instrument may be immensely increased by the use of a very long coil of wire, and by the addition of a second needle. The two needles are of equal size, and magnetised as nearly as possible to the same extent; they are then immovably fixed together parallel, and with their poles opposed, and hung by a long fibre of untwisted silk, with the lower needle in the coil, and the upper one above it. The advantage thus gained is twofold; the system is *astatic*, unaffected, or nearly so, by the magnetism of the earth; and the needles, being both acted upon in the same manner by the current, are urged with much greater force than one alone would be, all the actions of every part of the coil being strictly concurrent. A divided circle is placed below the upper needle, by which the angular motion can be measured, and the whole is enclosed in glass, to shield the needles from the agitation of the air. The arrangement is shown in fig. 66.

Fig. 66.



The direction of the current which deflects the galvanometer-needle in a particular way is easily determined by the rules given on page 106 when we know the direction in which the wire is coiled round the frame. For this purpose it is necessary to distinguish between *right-handed* and *left-handed* coils or helices. Suppose the wire to be coiled round a cylinder beginning at the left hand; then if the turns in front of the cylinder proceed from below upwards, as in fig. 67, the coil is left-handed; if, on the contrary, they proceed in front from above downwards, as in fig. 68, the coil is right-handed.

Fig. 67.

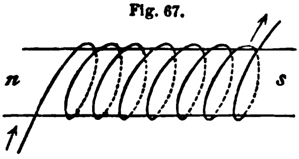
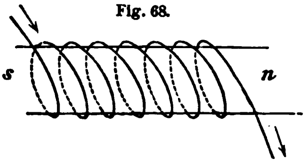


Fig. 68.



A magnetic needle placed with its centre in the axis of such a coil turns its north or south pole towards the end of the coil at which the current enters, according as the coil is left or right-handed.

The direction given to the needle is the same whether the coil is elongated, as in the above figures, or compressed, as in the galvanometer. As, however, in the galvanometer, when complete, it is not easy to see whether the coil is left or right-handed, it is best to determine by experiment, once for all, the direction taken by the needle when the current enters at one particular end of the coil.

Action of the Magnet on the Electric Current.—The action between the current and the magnet is mutual, so that if the conductor conveying the current is free to move, it is deflected in the direction opposite to that which the magnet takes under its influence; in short, if the magnet and conducting wire are both free to move, they place themselves at right angles to each other, the magnet moving in the manner indicated at page 106, and the wire in the opposite direction.

The action of the magnet on the current may be shown by means of Ampère's apparatus (fig. 69). On holding a bar-magnet below the rectangular wire, and parallel to its lower horizontal arm, the wire turns round and places itself at right angles to the magnet, the position of equilibrium being determined by the rule just alluded to.

A simpler apparatus for the purpose is De la Rive's floating battery, which consists of a pair of zinc and copper plates, contained in a wide glass tube attached to a cork float, and connected together by a rectangular wire, or a flat coil, or elongated helix of covered wire (fig. 70).

A movable electric current is deflected by the earth's magnetism in the same way as by an ordinary magnet. Thus the rectangular wire of Ampère's apparatus, or of a floating battery, when left to itself, will take up a position at right angles to the magnetic meridian; and remembering that the north magnetic pole of the earth is analogous to the south pole of an ordinary magnet, it is easy to see that, in the position of stable equilibrium, the direction of the current will be from east to west in the lower horizontal branch; and from below upwards on the western vertical side. If the wire has the form of a long helix, it will, in like manner, place itself with the turns of the helix at right angles to the magnetic meridian, and therefore with its axis parallel to that meridian, the ends pointing north and south, just like those of an ordinary magnetic needle. If the helix is left-handed, the end connected with the copper plate of the battery will point to the north.

Fig. 69.

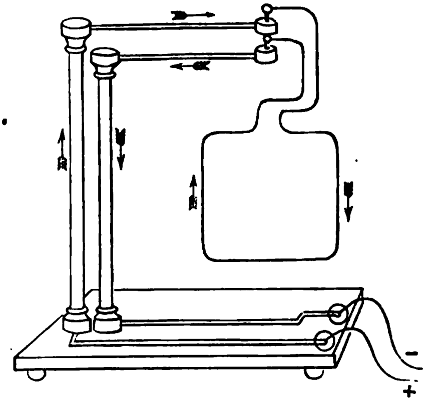
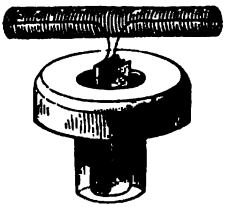


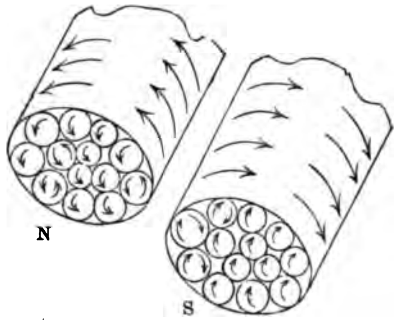
Fig. 70.



Mutual Action of Electric Currents.—If a conducting wire connecting the poles of a voltaic battery be brought near the movable wire of Ampère's apparatus, or the wire of a floating battery, the movable wire will be attracted or repelled according to the relative direction of the two currents, the general law of the action being that, *electric currents moving in parallel lines attract one another if they move in the same direction, and repel one another if they move in opposite directions.* From this it is easy to see that if a helix connecting the two poles of a battery be brought near the helix of a floating battery, and if the two helices are similar,—that is, both right or both left-handed,—their similar ends, *i.e.*, those by which the current enters or leaves the helix, will repel each other, and their dissimilar ends will attract each other, and consequently the moveable helix will place itself parallel to the fixed helix with its poles or ends in the contrary direction to those of the fixed helix. In short, the two helices will act on one another exactly like two bar magnets; and if an ordinary bar magnet be substituted for the fixed helix, the effect will still be the same, each end of the movable helix being attracted by one pole of the magnet, and repelled by the other.

This striking resemblance between the mutual action of electric currents and that of magnets has led to the idea, suggested and developed by Ampère, that magnetism is actually produced by electric currents circulating round the molecules of a magnet all in the same direction. These currents may be supposed to pre-exist in all magnetic bodies, even before the development of magnetic polarity, but to be disposed without regularity, so that they neutralise each other. Magnetisation is the process by which these molecular currents are made to move in one direction, those situated at the surface yielding, as their resultant, a finite current circulating round the magnet, while the currents in the interior are neutralised by those in the next external layer, the contiguous portions of which move in a direction opposite to their own. The resultant action of all these molecular currents is equivalent to that of a number of currents circulating round the magnet in planes perpendicular to its axis (fig. 71); and from what has been said about the mutual action of magnets and helices traversed by electric currents, it is easy to see that, on looking along the axis of a magnet with its *south* pole towards the observer, the current moves in the direction of the hands of a watch, that is, upwards on the left side, and downwards on the right.

Fig. 71.

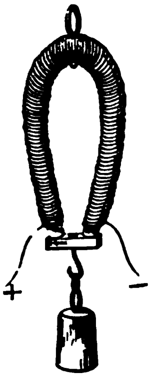


ELECTRO-DYNAMIC INDUCTION.

1. *Magnetisation by the Current.*—When an electro-current is passed through a wire placed at right angles to a bar of iron or steel, the bar acquires magnetic polarity, temporary in the case of soft iron, permanent in the case of hard iron or steel, the position of the poles being determined by the direction of the current, according to the laws already explained.

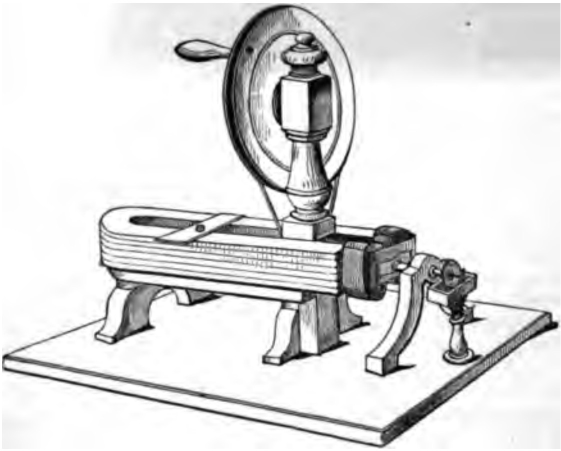
This effect is prodigiously increased by coiling the conducting wire in a helix round the bar. A piece of soft iron worked into the form of a horseshoe (fig. 72), and surrounded by a coil of wire covered with silk or cotton for the purpose of insulation, furnishes an excellent illustration of the inductive energy of the current in this respect: when the ends of the wire are put into communication with a small voltaic battery of a single pair of plates, the iron instantly becomes so highly magnetic as to be capable of sustaining a very heavy weight.

Fig. 72.



2. *Induction of Electric Currents by the action of Magnets, and of other Electric Currents.*—If the two extremities of the coil of the electro-magnet above described be connected with a galvanoscope, and the iron magnetised by the application of a permanent steel horse-shoe magnet to the ends of the bar, a momentary current will be developed in the wire, and pointed out by the movement of the needle. It lasts but a single instant, the needle, after a few oscillations, returning to a state of rest. On removing the magnet, whereby the polarity of the iron is at once destroyed, a second current or wave will become apparent, but in the opposite direction to that of the first. By employing a very powerful steel magnet, surrounding its iron keeper or armature with a very long coil of wire, and then making the armature itself rotate in front of the faces of the magnet,

Fig. 73.

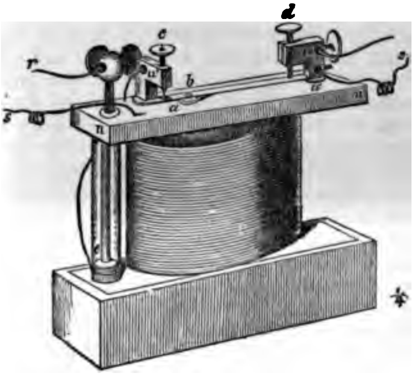


so that its induced polarity shall be rapidly reversed, magneto-electric currents may be produced, of such intensity as to give bright sparks and most powerful shocks, and exhibit all the phenomena of voltaic electricity. Fig. 73 represents a very powerful arrangement of this kind.

When two covered wires are twisted together or laid side by side for some distance, and a current transmitted through the one, a momentary electrical wave will be induced in the other in the reverse direction; and on breaking connection with the battery, a second single wave will become evident by the aid of the galvanoscope, in the same direction as that of the primary current. In the same way, when a current of electricity passes through one turn in a coil of wire, it induces two secondary currents in all the other turns of the coil; the first current, which is induced when the circuit is closed, moves in the opposite direction to the primary current; the second, which comes in existence when the circuit is broken, has a motion in the same direction as the primary current. The effect of the latter is added to that of the primary current. Hence, if a wire coil be made part of the conducting wire of a weak electric pile, and if the primary current, by means of an appropriate arrangement, be made and broken in rapid succession, we can increase in a remarkable manner the effects which are produced at the moment of breaking the circuit, either at the place of interruption, such as the spark-discharges, or in secondary closing conductors, as in the action on the nerves, or in the decomposition of water.

If the two copper wires, the one above the other, be twisted round the same hollow cylinder, and one of these wires—the inner one, for instance,—be made part of a galvanic circuit, a current of short duration is induced in the outer wire, both by making and by breaking contact. The strength of this current can be very appreciably increased by filling the hollow cylinder with a bundle of thin iron rods, whereby magnetic and electrical induction are made to co-operate. The more frequently contact is alternately made and broken, the greater is the number of induced currents that follow each other, and the more powerful, within certain limits, is the action. By an ingenious contrivance, the invention of Dr. Neef, in which contact is made and broken by the current itself, the induction apparatus actually becomes an electrical machine. Fig. 74 exhibits the original apparatus slightly modified. The arrangement consists essentially of an elastic copper strip *a a′*, which is fixed at *a′*, and carries at *b* a small plate of soft iron. The latter hangs over the iron rods of the induction coil, which are somewhat raised in this particular point, but without touching them. The end *a* of the copper strip is covered with a little plate of platinum, which presses against a platinum point of the screw *c*. The current having traversed the inner coil, passes from the point *c* to the plate *a*, in order to return through the copper strip *a a′* and the wire *s*. By the passage of the current the iron rods have become magnetic and attract the iron plate *b*, whereby the end *a* of the copper strip is removed from the platinum point, and contact is broken. But as soon as the current ceases, the iron rods lose their magnetism, the elastic copper strip returns to its former position, and establishes again the current for a short time. The screws *c* and *d* regulate the position of the spring and the time of its oscillations, the velocity of which may be estimated by the pitch of the notes produced. This apparatus, called an induction coil, which was first made by Dr. Neef, in 1830, has been considerably improved within the last few years. Ruhmkorff especially, by a more perfect isolation of the wire coils, has succeeded to a much greater extent in preserving the electrical induction. He has thus obtained a state of electrical tension which resembles that produced by frictional electricity, capable of giving long sparks, and shocks of unendurable force. By means of Ruhmkorff's coil, Grove has effected decompositions in water and other bad-conducting liquids, which resemble those obtained many years ago by Wollaston by means of the electrical machine. These phenomena of decomposition, which in water, for instance, furnish oxygen and hydrogen at the same pole, must be distinguished from true electro-chemical decompositions; they are, in fact, effects of heat, as Grove has pointed out.

Fig. 74.



THERMO-ELECTRICITY.

In the year 1822 Professor Seebeck of Berlin discovered a new source of electricity, namely, inequality of temperature and conducting power in different metals placed in contact, or in the same metal in different states of compression and density.

Where two pieces of different metals, connected together at each end, have one of their joints more heated than the other, an electric current is immediately set up. Of all the metals tried, bismuth and antimony form the most powerful combination. A single pair of bars having one of their junctions heated in the manner shown in fig. 75 can develope a current strong enough to deflect a compass needle placed within; and, by arranging a number in a series and heating their alternate ends, the intensity of the current may be very much increased. Such an arrangement, represented in fig. 76, is called a thermo-electric pile.

Fig. 75.

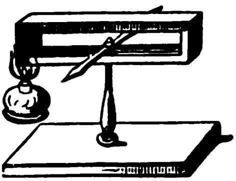
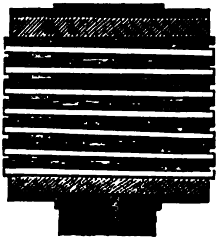


Fig. 76.



The current produced by this instrument, even with a great number of alterations, is exceedingly feeble when compared with that produced by the voltaic pile; but the thermomultiplier placed in contact with a delicate galvanoscope forms an instrument for measuring small variations of temperature, far surpassing in delicacy the most sensitive air-thermometer: it has rendered most important service in the study of radiant heat.

ANIMAL ELECTRICITY.

Certain fishes, as the torpedo or electric ray and the electric eel (*Gymnotus electricus*), of South America, are furnished with a special organ or apparatus for developing electric force, which is employed in defence, or in the pursuit of prey. Electricity is here seen to be closely connected with nervous power; the shock is given at the will of the animal, and great exhaustion follows repeated exertion of the power.

PART II.

CHEMISTRY OF ELEMENTARY BODIES.

It is convenient for many reasons to commence the study of the elementary bodies with those which enter into the composition of air and water.

OXYGEN.

Atomic weight, 16.—Symbol, O.

Oxygen was discovered in the year 1774, by Scheele, in Sweden, and Priestley, in England, independently of each other, and described under the terms *empyreal air* and *dephlogisticated air*. The name oxygen* was given to it by Lavoisier some time afterwards. Oxygen exists in a free and uncombined state in the atmosphere, mixed with another gaseous body, nitrogen. No very good direct means exist, however, for separating it from the latter; and, accordingly, it is always obtained for purposes of experiment by decomposing certain of its compounds, which are very numerous.

The red oxide of mercury, or *red precipitate* of the old writers, may be employed for this purpose. In this substance the attraction which holds together the mercury and the oxygen is so feeble, that simple exposure to heat suffices to bring about decomposition.

The red precipitate is placed in a short tube of hard glass, to which is fitted a perforated cork, furnished with a piece of narrow glass tube, bent as in fig. 77. The heat of a spirit-lamp being applied to the substance, decomposition speedily commences, and globules of metallic mercury collect in the cool part of the wide tube, which answers the purpose of a retort, while gas issues in considerable quantity from the apparatus. This gas is collected and examined by the aid of the pneumatic trough, which consists of a vessel of water provided with a shelf, upon which stand the jars or bottles destined to receive the gas, filled with water and inverted. By keeping the level of the liquid above the mouth of the jar, the water is retained in the latter by the pressure of the atmosphere, and entrance of air is prevented. When the jar is brought over the extremity of the gas-delivery tube, the bubbles of gas, rising through the water, collect in the upper part of the jar, and displace the liquid. As soon as one jar is filled, it may be removed, still keeping its mouth below the water-level, and another substituted. The whole arrangement is shown in fig. 77.

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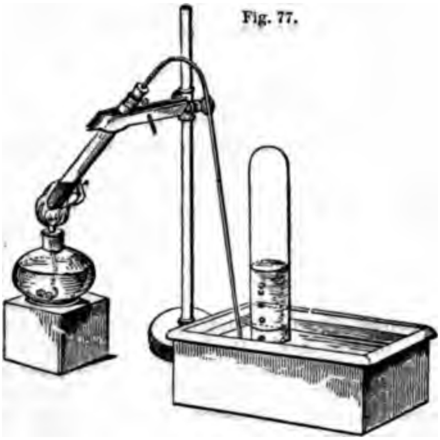
* From ὀξὺ, acid, and γεν, a root signifying production.

Fig. 77.



The experiment here described is more instructive as an instance of the resolution by simple means of a compound body into its constituents, than valuable as a source of oxygen gas. A better and more economical method is to expose to heat in a retort, or flask furnished with a bent tube, a portion of the salt called potassium chlorate. A common Florence flask serves perfectly well, the heat of the spirit-lamp being sufficient. The salt melts and decomposes with ebullition, yielding a very large quantity of oxygen gas, which may be collected in the way above described. The first portion of the gas often contains a little chlorine. The white saline residue in the flask is potassium chloride. This plan, which is very easy of execution, is always adopted when very pure gas is required for analytical purposes.

A third method, very good when perfect purity is not demanded, is to heat to redness, in an iron retort or gun-barrel, the black manganese oxide of commerce, which under these circumstances suffers decomposition, although not to the extent manifest in the red precipitate.

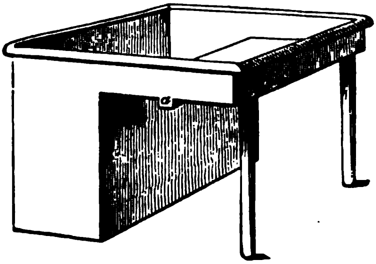
If a little of the black manganese oxide be finely powdered and mixed with potassium chlorate, and this mixture heated in a flask or retort by a lamp, oxygen will be disengaged with the utmost facility, and at a far lower temperature than when the chlorate alone is used. All the oxygen comes from the chlorate, the manganese remaining quite unaltered. The materials should be well dried in a capsule before their introduction into the flask. This experiment affords an instance of an effect by no means rare, in which a body seems to act by its mere presence, without taking any obvious part in the change brought about.

Methods for the preparation of oxygen on a large scale will be found described under the heads of sulphuric acid and barium dioxide.

Whatever method be chosen—and the same remark applies to the collection of all other gases by similar means—the first portions of gas must be suffered to escape, or be received apart, as they are contaminated by the atmospheric air of the apparatus.

The practical management of gases is a point of great importance to the chemical student, and one with which he must endeavour to familiarise himself. The water-trough just described is one of the most indispensable articles of the laboratory, and by its aid all experiments on gases are carried on when the gases themselves are not sensibly acted upon by water. The trough is best constructed of japanned copper, the form and dimensions being regulated by the magnitude of the jars. It should have a firm shelf, so arranged as to be always about an inch below the level of the water, and in the shelf a groove should be made about half an inch in width, and the same in depth, to admit the extremity of the delivery-tube beneath the jar, which stands securely upon the shelf. When the pneumatic trough is required of tolerably large dimensions, it may with great advantage have the form and dispositions represented in fig. 78. The end of the groove spoken of, which crosses the shelf or shallow portion, is shown at *a*.

Fig. 78.

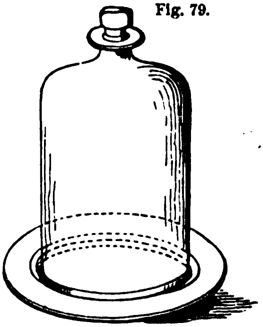


Gases are transferred from jar to jar with the utmost facility, by first filling the vessel, into which the gas is to be passed, with water, inverting it, carefully retaining its mouth below the water-level, and then bringing beneath it the aperture of the jar containing the gas. On gently inclining the latter, the gas passes by a kind of inverted decantation into the second vessel. When the latter is narrow, a funnel may be placed loosely in its neck, by which loss of gas will be prevented.

A jar wholly or partially filled with gas at the pneumatic trough may be removed by placing beneath it a shallow basin, or even a common plate, so as to carry away enough water to cover the edge of the jar; and many gases, especially oxygen, may be so preserved for many hours without material injury.

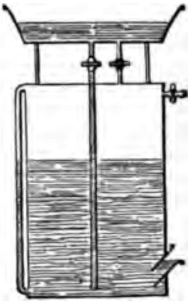
Gas-jars are often capped at the top, and fitted with a stop-cock for transferring gas to bladders or caoutchouc bags. When such a vessel is to be filled with water, it may be slowly sunk in an upright position in the well of the pneumatic trough, the stop-cock being open to allow the air to escape, until the water reaches the brass cap. The cock is then to be turned, and the jar lifted upon the shelf, and filled with gas in the usual way. If the trough be not deep enough for this method of proceeding, the mouth may be applied to the stop-cock, and the vessel filled by sucking out the air until the water rises to the cap. In all cases it is proper to avoid as much possible wetting the stop-cocks, and other brass apparatus.

Fig. 79.



Mr. Pepys contrived many years ago, an admirable piece of apparatus for storing and retaining large quantities of gas. It consists of a drum or reservoir of sheet copper, surmounted by a shallow trough or cistern, the communication between the two being made by a couple of tubes furnished with stop-cocks, one of which passes nearly to the bottom of the drum, as shown in fig. 80. A short wide open tube is inserted obliquely near the bottom of the vessel, into which a plug may be tightly screwed. A stop-cock near the top serves to transfer gas to a bladder or tube-apparatus. A glass water-gauge affixed to the side of the drum, and communicating with both top and bottom, indicates the level of the liquid within.

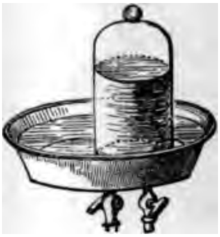
Fig. 80.



To use the gas-holder, the plug is first to be screwed into the lower opening, and the drum completely filled with water. All three stop-cocks are then to be closed and the plug removed. The pressure of the atmosphere retains the water in the gas-holder, and if no air-leakage occurs, the escape of water is inconsiderable. The extremity of the delivery-tube is now to be well pushed through the open aperture into the drum, so that the bubbles of gas may rise without hindrance to the upper part, displacing the water, which flows out in the same proportion into a vessel placed for its reception. When the drum is filled, or enough gas has been collected, the tube is withdrawn and the plug screwed into its place.

When a portion of the gas is to be transferred to a jar, the latter is to be filled with water at the pneumatic trough, carried by the help of a basin or plate to the cistern of the gas-holder, and placed over the shorter tube. On opening the cock of the neighbouring tube, the hydro-static pressure of the column of water will cause compression of the gas, and increase its elastic force, so that, on gently turning the cock beneath the jar, it will ascend into the latter in a rapid stream of bubbles. The jar, when filled, may again have the plate slipped beneath it, and be removed without difficulty.

Fig. 81.



Properties of Oxygen.—Oxygen, when free or uncombined, is known only in the gaseous state, all attempts to reduce it to the liquid or solid condition by cold and pressure having completely failed. When pure, it is colourless, tasteless, and inodorous.

Oxygen is, bulk for bulk, a little heavier than atmospheric air, its specific gravity being 1·10563, referred to that of air as unity, and 16 referred to that of hydrogen as unity. A litre of oxygen at the standard temperature and pressure, that is to say, at 0° C., and 760 millimeters barometric pressure, weighs 1·43028 gram. At 15·5° C. (60° F.), and under a pressure of 30 inches, 100 cubic inches of the gas weigh 34·29 grains.

Oxygen is the sustaining principle of animal life, and of all the ordinary phenomena of combustion. Bodies which burn in the air, burn with greatly increased splendour in oxygen gas. If a taper be blown out, and then introduced while the wick remains red-hot, it is instantly rekindled: a slip of wood or a match is relighted in the same manner. This effect is highly characteristic of oxygen, there being but one other gas which possesses the same property; and this is easily distinguished by other means. The experiment with the match is also constantly used as a rude test of the purity of the gas when it is about to be collected from the retort, or when it has stood for some time in contact with water exposed to air.

When a bit of charcoal is affixed to a wire, and plunged with a single point red-hot into a jar of oxygen, it burns with great brilliancy, throwing off beautiful scintillations, until, if the oxygen be in excess, it is completely consumed. An iron wire, or, still better, a steel watch-spring, armed at its extremity with a bit of lighted amadou, and introduced into a vessel of oxygen gas, exhibits a most beautiful phenomenon of combustion. If the experiment be made in a jar standing on a plate, the fused globules of black iron oxide fix themselves in the glaze of the latter, after falling through a stratum of water half an inch in depth. Kindled sulphur burns with great beauty in oxygen; and phosphorus, under similar circumstances, exhibits a splendour which the eye is scarcely able to support. In each case the burning body enters into combination with the oxygen, forming a compound called an oxide.

When a body burns in oxygen gas the same ultimate effect is produced as in atmospheric air; the action is, however, more energetic, from the absence of the gas which, in the air, dilutes the oxygen and enfeebles its chemical powers. The process of respiration in animals is an effect of the same nature as common combustion. The blood contains substances which slowly burn by the aid of the oxygen thus introduced into the system. When this action ceases, life becomes extinct.

Ozone.—It has long been known that dry oxygen, or atmospheric air, when exposed to the action of a series of electric sparks, emits a peculiar and somewhat metallic odour. The same odour may be imparted to moist oxygen by allowing phosphorus to remain for some time in it, and by several other processes. A more accurate examination of this odorous air has shown that, in addition to the smell, it possesses several properties not exhibited by oxygen in its ordinary state. One of its most characteristic effects is the liberation of iodine from potassium iodide. This odorous principle has been the subject of many researches, in particular by Schönbein, of Basle, who proposed for it the name of ozone.*

An easy method of exhibiting the production of ozone is to transmit a current of oxygen through a tube into which a pair of platinum wires is sealed, with the points at a little distance apart; on connecting one of the wires with the prime conductor of an electrical machine in good action, and the other with the ground, the characteristic odour of ozone is immediately developed in the issuing gas; but, notwithstanding the powerful odour thus produced, only a small portion of the oxygen undergoes this change. Andrews and Tait have shown that, to obtain the maximum of ozone, it is necessary to transmit the discharge silently, between very fine points; if sparks are allowed to pass, a considerable portion of the ozone is reconverted into ordinary oxygen as fast as it is formed. Siemens prepares ozone by induction: he forms a sort of Leyden jar, by coating the interior of a long tube with tin-foil, and passes over this tube a second wider tube coated with tin-foil on its outer surface. Between the two tubes a current of pure dry oxygen is passed, which becomes electrified by induction, on connecting the inner and outer coating with the terminal wires of an induction-coil; by this means it is said that from 10 to 15 per cent. of the oxygen may be converted into ozone.

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* From ὄζειν, to emit an odour.

Ozone may also be obtained in several ways, without the aid of electricity; thus it is formed in small quantity when a stick of phosphorus is suspended in a bottle filled with moist air; in the electrolytic decomposition of water; and by the action of strong sulphuric acid on potassium permanganate. There has been considerable discussion about the nature and composition of ozone; but the most trustworthy experiments seem to show that, in whatever way produced, it is merely a modified form of oxygen.

Ozone is insoluble in water and in solutions of acids or alakalies, but is absorbed by a solution of potassium iodide. Air charged with it exerts an irritating action on the lungs. Ozone is decomposed by heat, gradually at 100°, instantly at 290°. It is an extremely powerful oxidising agent; possesses strong bleaching and disinfecting powers; corrodes cork, caoutchouc, and other organic substances; and rapidly oxidises iron, copper, and even silver when moist, as well as dry mercury and iodine. It is remarkable that the absorption of ozone by these and other agents is not attended with any contraction of volume. The explanation of this fact appears to be, that oxygen when ozonised diminishes in volume (in the proportion of 3 to 2, according to Soret), and that when the ozone is decomposed by a metal or other substance, one portion of it enters into combination, while the remainder, which is set free as ordinary oxygen, occupies the same bulk as the ozone itself.

The most delicate test for the presence of ozone in any gas is afforded by a strip of paper moistened with a mixture of starch and solution of potassium iodide. On exposing such paper to the action of ozone, the potassium iodine is decomposed, its potassium combining with oxygen, while the iodide is liberated, and forms a deep blue compound with the starch. Now, when paper thus prepared is exposed to the open air for five or ten minutes, it often acquires a blue tint, the intensity of which varies on different days. Hence it is supposed that ozone is present in the air in variable quantity. But iodine may be liberated from potassium iodide by many other agents, especially by certain oxides of nitrogen, which are very likely to be present in the air in minute quantities: hence the existence of ozone in the air cannot be proved by this reaction alone.

Houzeau has, however, shown that a solution of potassium iodide exposed to the air in the open country becomes alkaline; an effect which cannot be attributed to nitrous acid. Moreover, Andrews finds that the constituent of the air which separates iodine from potassium iodide is destroyed by the same influences as ozone, viz., by a temperature of 237°, or by contact with manganese dioxide and other peroxides. The presence of ozone in the air can therefore no longer be doubted.

Oxides.—General Laws of Chemical Combination.—Chemical Nomenclature and Notation.—The compounds formed by the union of oxygen with other bodies bear the general name of oxides; they are very numerous and important. They are conveniently divided into three principal groups or classes. The first division contains all those oxides which resemble in their chemical relations the oxides of potassium, sodium, silver, or lead: these are denominated alkaline or basic oxides. The oxides of the second group have properties opposed to those of the bodies mentioned; the oxides of sulphur and phosphorus may be taken as typical representatives of the class; they are called acid oxides, and are capable of uniting with the basic oxides, and forming compounds called salts. Thus, when the oxide of sulphur, called sulphuric oxide, is passed in the state of vapour over heated barium oxide, combination takes place, attended with vivid incandescence, and a salt called barium sulphate is produced, containing all the elements of the two original bodies, namely, barium, sulphur, and oxygen.

There is also an intermediate group of oxides called neutral oxides, from their slight disposition to enter into combination. The black oxide of manganese, already mentioned, is an excellent example. It must not be supposed, however, that the three groups of oxides just mentioned are separated from each other by decided lines of demarcation; on the contrary, they blend into one another by imperceptible degrees, and the same oxide may, in many cases, exhibit either acid or basic relations, according to the circumstances under which it is placed.

Among salts there is a particular group, namely, the hydrogen salts, containing the elements of an acid oxide and water (hydrogen oxide), which are especially distinguished as acids, because many of them possess in an eminent degree the properties to which the term acid is generally applied, such as a sour taste, corrosive action, solubility in water, and the power of reddening certain blue vegetable colours. A characteristic property of these acids, or hydrogen salts, is their power of exchanging their hydrogen for a metal presented to them in the free state, or in the form of oxide. Thus, sulphuric acid, which contains sulphur, oxygen, and hydrogen, readily dissolves metallic zinc, the metal taking the place of the hydrogen, which is evolved as gas, and forming a salt containing sulphur, oxygen, and zinc; in fact, a *zinc sulphate*, produced from a *hydrogen sulphate* by substitution of zinc for hydrogen. The same substitution and formation of zinc sulphate take place when zinc oxide is brought into contact with sulphuric acid; but in this case the hydrogen, instead of being evolved as gas, remains combined with the oxygen derived from the zinc oxide, forming water.

A series of oxides containing quantities of oxygen in the proportion of the numbers 1, 2, 3, united with a constant quantity of another element, are distinguished as *monoxide*, *dioxide*, and *trioxide* respectively, the Greek numerals indicating the several degrees of oxidation. A compound, intermediate between a monoxide and a dioxide is called a *sesquioxide*, *e.g.* :—

	Chromium.		Oxygen.
Chromium monoxide, ...	52·5	+	16
Chromium sesquioxide, ...	52·5	+	24
Chromium dioxide, ...	52·5	+	32
Chromium trioxide, ...	52·5	+	48

When a metal forms two basic or salifiable oxides, they are distinguished by adjectival terms, ending in *ous* for the lower, and *ic* for the higher degree of oxidation, *e.g.* :—

	Iron.		Oxygen.
Iron monoxide, or Ferrous oxide, . .	56	+	16
Iron sesquioxide, or Ferric oxide, . .	56	+	24

The salts resulting from the action of acids on these oxides are also distinguished as ferrous and ferric salts respectively.

Acid oxides of the same element, sulphur for example, are also distinguished by the terminations *ous* and *ic*, applied as above; their acids, or hydrogen salts, receive corresponding names; and the salts formed from these acids are distinguished by names ending in *ite* and *ate* respectively. Thus, for the oxides and salts of sulphur :—

	Sulphur.		Oxygen.		
Sulphurous oxide, ...	32	+	32		
Hydrogen sulphite, or Sulphurous acid,	32	+	48	+	Hydrogen. 2
Lead sulphite, ...	32	+	48	+	Lead. 207
Sulphuric oxide, ...	32	+	48		
Hydrogen sulphate, or Sulphuric acid,	32	+	64	+	Hydrogen. 2
Lead sulphate	32	+	64	+	Lead. 207

The acids above spoken of are oxygen-acids; and formerly it was supposed that all acids contained oxygen—that element being, indeed, regarded as the acidifying principle: hence its name (p. 116). At present, however, we are acquainted with many bodies which possess all the characters above specified as belonging to an acid, and yet do not contain oxygen. For example, hydrochloric acid (formerly called muriatic acid, or spirit of salt)—which is a hydrogen chloride or compound of hydrogen and chlorine—is intensely sour and corrosive; reddens litmus strongly; dissolves zinc, which drives out the hydrogen and takes its place in combination with the chlorine, forming zinc chloride; and dissolves most metallic oxides, exchanging its hydrogen for the metal, and forming a metallic chloride and water.

Bromine, iodine, and fluorine, also form, with hydrogen, acid compounds analogous in every respect to hydrochloric acid.

Compounds of chlorine, bromine, iodine, fluorine, sulphur, selenium, phosphorus, &c., with hydrogen and metals, are grouped, like the oxygen-compounds, by names ending in *ide:* thus we speak of zinc chloride, calcium fluoride, hydrogen sulphide, copper phosphide, &c. The numerical prefixes, *mono, di, tri*, &c., as also the terminations *ous* and *ic*, are applied to these compounds in the same manner as to the oxides, thus—

	Hydrogen.		Bromine.
Hydrogen bromide,	1	+	80
	Potassium.		Sulphur.
Potassium monosulphide,	78·2	+	32
Potassium disulphide,	78·2	+	64
Potassium trisulphide,	78·2	+	96
Potassium tetrasulphide,	78·2	+	128
Potassium pentasulphide,	78·2	+	160
	Iron.		Chlorine.
Ferrous chloride,	56	+	71
Ferric chloride,	56	+	105·5
	Tin.		Sulphur.
Stannous sulphide,	118	+	64
Stannic sulphide,	118	+	128

The Latin prefixes *uni, bi, ter, quadro*, &c., are often used instead of the corresponding Greek prefixes; there is no very exact rule respecting their use; but, generally speaking, it is best to employ a Greek or Latin prefix, according as the word before which it is placed is of Greek or Latin origin. Thus, *di*oxide corresponds with *bi*sulphide; on the whole, however, the Greek prefixes are most generally employed.

The composition of these oxides and sulphides affords an illustration of a law which holds good in a large number of instances of chemical combination, viz., that *when two bodies*, A *and* B, *are capable of uniting in several proportions, the several quantities of* B *which combine with a given or constant quantity of* A *stand to one another in very simple ratios.* Thus, the several quantities of sulphur which unite with a given quantity (78·2 parts) of potassium are to one another as the numbers

1, 2, 3, 4, 5;

and the quantities of oxygen which unite with a given quantity of chromium are as the numbers

1, 1½, 2, 3,
or 2, 3, 4, 6.

It must be especially observed that no compounds are known intermediate in composition between those which are represented by these numbers. There is no oxide of chromium containing $1\frac{1}{4}$ or $1\frac{5}{8}$ or $2\frac{7}{8}$ times as much oxygen as the lowest; no sulphide of potassium the quantity of sulphur in which is expressed by any fractional multiple of the lowest. The quantities of the one element which can unite with a constant quantity of the other, increase, not continuously, but by successive and well-defined steps or increments, standing to one another, for the most part, in simple numerical ratios.

This is called the "Law of Multiples." The observation of it has led to the idea that the elementary bodies are composed of ultimate or indivisible particles or atoms, each having a constant weight peculiar to itself (the atomic weights given in the table on page 3) and that combination between two elements takes place by the juxtaposition of these atoms. A collection of elementary atoms united together to form a compound constitutes a molecule, the weight of which is equal to the sum of the weights of its component atoms. Thus an atom of chlorine weighing 35·5 unites with an atom of hydrogen weighing 1, to form a molecule of hydrogen-chloride weighing 36·5. An atom of oxygen weighing 16 unites with 2 atoms of hydrogen, each weighing 1, to form a molecule of water, weighing $16+2 . 1=18$. An atom of oxygen, weighing 16, unites with an atom of lead, weighing 207, to form a molecule of lead oxide, weighing 223. Two atoms of potassium, each weighing 39·1, unite with 1, 2, 3, 4, and 5 atoms of sulphur, each weighing 32, to form the several sulphides enumerated on page 123.

These combinations are represented symbolically by the juxtaposition of the symbols of the elementary atoms given in the table already referred to; thus the molecule of hydrogen chloride, composed of 1 atom of hydrogen and 1 atom of chlorine, is represented by the symbol or formula HCl; that of water (2 atoms of hydrogen and 1 atom of oxygen), by HHO, or more shortly H_2O. In like manner the different oxides and sulphides, acids and salts above enumerated, are represented symbolically as follows:—

Chromium monoxide, . . .	CrO	
Chromium sesquioxide, . .	CrCrOOO	or Cr_2O_3
Chromium dioxide, . . .	CrOO	or $Cr\,O_2$
Chromium trioxide, . . .	CrOOO	or $Cr\,O_3$
Sulphurous oxide, ...	SOO	or SO_2
Hydrogen sulphite or Sulphurous acid, ...	SOOOHH	or $SO_3\,H_2$
Lead sulphite, ...	SOOOPb	or $SO_3\,Pb$
Potassium monosulphide, . .	KKS	or K_2S
Potassium disulphide, . . .	KKSS	or $K_2\,S_2$
Potassium trisulphide, . . .	KKSSS	or $K_2\,S_3$
Potassium tetrasulphide, . .	KKSSSS	or $K_2\,S_4$
Potassium pentasulphide, . .	KKSSSSS	or $K_2\,S_5$

A group of two or more atoms of the same element is denoted by placing a numeral either before the symbol, or, as in the preceding examples, a small numeral to the right of the symbol, and either above or below the line; thus OOO may be abbreviated into 3O, or O^3, or O_3.

The multiplication of a group of dissimilar atoms is denoted by placing a numeral to the left of the group of symbols, or by enclosing them in brackets, and placing a small numeral to the right: thus, 3HCl or $(HCl)_3$ denotes 3 molecules of hydrogen chloride; $2H_2SO_4$ denotes 2 molecules of hydrogen sulphate.

The combination of two groups or molecules is denoted by placing their symbols in juxtaposition, with a dot between them: thus $ZnO.SO_3$ denotes a compound of zinc oxide with sulphur trioxide; $K_2O.H_2O$, a compound of potassium oxide with hydrogen oxide or water. Sometimes a comma or the sign + is used instead of the dot. To express the multiplication of such a group, the whole is enclosed in brackets, and a numeral placed on the left; *e.g.* $2(ZnO.SO_3)$; $3(K_2O.H_2O)$, &c. If the brackets were omitted, the numeral would affect only the symbols to the left of the dot; thus $3K_2O.H_2O$ signifies 3 potassium oxide and 1 water, not 3 potassium oxide and 3 water.*

Equivalents.—It has been already stated that elements can replace one another in combination; thus, when hydrogen chloride is placed in contact with zinc, the zinc dissolves and enters into combination with the chlorine, while a quantity of hydrogen is evolved as gas. Now this substitution of zinc for hydrogen always takes place in definite proportion by weight, 32·6 parts of zinc being dissolved for every 1 part of hydrogen expelled. In like manner when potassium is thrown into water, hydrogen is evolved and the potassium dissolves, 39·1 parts of the metal dissolving for every 1 part of hydrogen given off. Again, if silver be dissolved in nitric acid, and metallic mercury immersed in the solution, the mercury will be dissolved and will displace the silver, which will be separated in the metallic state; and for every 100 parts of mercury dissolved 108 parts of silver will be thrown down. In like manner copper will displace the mercury in the proportion of 31·75 parts of copper to 100 of mercury, and iron will displace the copper in the proportion of 28 parts of iron to 31·75 parts of copper.

These are particular cases of the general law, that, *when one element takes the place of another in combination, the substitution or replacement always takes place in fixed or definite proportions.* The relative quantities of different elements which thus replace one another, are called chemical equivalents or equivalent numbers; they are either identical with the atomic weights, or simple multiples, or submultiples of them. For example, in the substitution of potassium for hydrogen, and of copper for mercury, and of iron for copper, the equivalents are to one another in the same proportion as the atomic weights, as may be seen by comparing the numbers just given with those in the table on page 3. In the substitution of zinc for hydrogen, on the other hand, the quantity of zinc which takes the place of 1 part of hydrogen is only half the atomic weight; similarly in the substitution of mercury for silver.

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* The neglect of this distinction often leads to considerable confusion in chemical notation.

All chemical reactions consist either in the direct addition or separation of elements, or in substitutions like those just noticed, the latter being by far the most frequent form of chemical change.

Chemical Equations.—Chemical reactions may be represented symbolically in the form of equations, the symbols of the reacting substances being placed on the left hand, and those of the new substances resulting from the change, on the right: for example—

1. Resolution of mercuric oxide by heat into mercury and oxygen—

$$HgO = Hg + O$$

2. Resolution of manganese dioxide by heat into maganoso-manganic oxide and oxygen—

$$3MnO_2 = Mn_3O_4 + O_2$$

3. Action of zinc on hydrogen chloride, producing zinc chloride and free hydrogen—

$$2HCl + Zn = ZnCl_2 + H_2$$

4. Action of zinc on hydrogen sulphate, producing zinc sulphate and hydrogen—

$$H_2SO_4 + Zn = ZnSO_4 + H_2$$

5. Action of zinc oxide on hydrogen chloride or sulphate, producing zinc chloride or sulphate and water—

$$2HCl + ZnO = ZnCl_2 + H_2O,$$

and

$$H_2SO_4 + ZnO = ZnSO_4 + H_2O.$$

It need scarcely be observed that the test of correctness of such an equation is, that the number of atoms of the elements on one side should be equal to the number of atoms of the same element on the other side

Any such symbolical equation may be converted into a numerical equation, by substituting for each of the chemical symbols its numerical value from the table of atomic weights.

The laws of chemical action and their expression by symbols and equations will receive abundant illustration in the special descriptions which follow; their general consideration will also be more fully developed in a subsequent part of the work.

HYDROGEN.

Atomic weight, 1; symbol, H.

Hydrogen may be obtained for experimental purposes by deoxidising water, of which it forms a characteristic component.*

If a tube of iron or porcelain, containing a quantity of filings or turnings of iron, be fixed across a furnace, and its middle portion be made red-hot, and then the vapour of water passed over the heated metal, a large quantity of permanent gas will be disengaged from the tube, and the iron will be converted into oxide, and acquire an increase in weight. The gas is hydrogen; it may be collected over water and examined.

Hydrogen is, however, more easily obtained by decomposing hydrochloric or dilute sulphuric acid with zinc, the metal then displacing the hydrogen in the manner already explained (p 128).

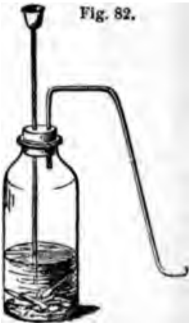

Fig. 82.

The simplest method of preparing the gas is the following:—A wide-necked bottle is chosen, and fitted with a sound cork, perforated by two holes for the reception of a small tube-funnel reaching nearly to the bottom of the bottle, and a piece of bent glass† tube to convey away the disengaged gas. Granulated zinc, or scraps of the malleable metal, are put into the bottle, together with a little water, and sulphuric acid slowly added by the funnel, the point of which should dip into the liquid. The evolution of gas is easily regulated by the supply of acid; and when enough has been discharged to expel the air of the vessel, it may be collected over water in a jar, or passed into a gas-holder. In the absence of zinc, filings of iron or small nails may be used, but with less advantage.

Hydrogen is colourless, tasteless, and inodorous when quite pure.

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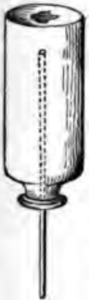
* Hence the name, from ὕδωρ, water, and γεν.

† A little practice will soon enable the pupil to construct and arrange a variety of useful forms of apparatus, in which bottles, and other articles always at hand, are made to supersede more costly instruments. Glass tube, purchased by weight of the maker, may be cut by scratching with a file, and then applying a little force with both hands. It may be softened and bent, when of small dimensions, by the flame of a spirit-lamp, or a candle, or, better, by a gas jet. Corks may be perforated by a heated wire, and the hole rendered smooth and cylindrical by a round file; or the ingenious cork-borer of Dr. Mohr, now to be had of all instrument makers, may be used instead. Lastly, in the event of bad fitting, or unsoundness in the cork itself, a little yellow wax melted over the surface, or even a little grease applied with the finger, renders it sound and air-tight, when not exposed to heat.

To obtain it in this condition, it must be prepared from the purest zinc that can be obtained, and passed in succession through solutions of potash and silver nitrate. When prepared from commercial zinc, it has a slight smell, which is due to impurity, and when iron has been used, the odour is very strong and disagreeable. It is inflammable, and burns, when kindled, with a pale yellowish flame, evolving much heat, but very little light. The product of the combustion is water. Hydrogen is even less soluble in water than oxygen, and has never been liquefied. Although destitute of poisonous properties, it is incapable of sustaining life.

Fig. 83.



Hydrogen is the lightest substance known; Dumas and Boussingault place its density between 0·0691 and 0·0695, referred to that of air as unity. The weight of a litre of hydrogen at 0° C., and under a barometric pressure of 0·760 meter, is 0·8961 gram: consequently a gram of hydrogen occupies a space of 11·15947 liters.* At 15·5° C. (60° F.) and 30 inches barometric pressure, 100 cubic inches weigh 2·14 grains.

When a gas is much lighter or much heavier than atmospheric air, it may often be collected and examined without the aid of the pneumatic trough. A bottle or narrow jar may be filled with hydrogen without much admixture of air, by inverting it over the extremity of an upright tube delivering the gas. In a short time, if the supply be copious, the air will be wholly displaced, and the vessel filled. It may now be removed, the vertical position being carefully retained, and closed by a stopper or a glass plate. If the mouth of the jar be wide, it must be partially closed by a piece of cardboard during the operation. This method of collecting gases by displacement is often extremely useful.

Hydrogen was formerly used for filling air-balloons, being made for the purpose on the spot from zinc or iron and dilute sulphuric acid. Its use is now superseded by that of coal-gas, which may be made very light by employing a high temperature in the manufacture. Although far inferior to pure hydrogen in buoyant power, it is found in practice to possess advantages over that substance, while its greater density is easily compensated by increasing the size of the balloon.

Diffusion of Gases.—There is a very remarkable property possessed by gases and vapours in general, which is seen in a high degree of intensity in the case of hydrogen; this is what is called diffusive power. If two bottles containing gases which do not act chemically upon each other at common temperatures be connected by a narrow tube and left for some time, the gases will be found, at the expiration of a certain time, depending much upon the narrowness of the tube and its length, uniformly mixed, even though they differ greatly in density, and the system has been arranged in a vertical position, with the heavier gas downwards. Oxygen and hydrogen can thus be made to mix, in a few hours, against the action of gravity, through a tube a yard in length, and not more than one quarter of an inch in diameter: and the same is true of all other gases which are destitute of direct action upon each other.

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* As a near approximation, it may be remembered that a liter of hydrogen weighs 0·09 gram, or 9 centigrams, and a gram of hydrogen occupies 11·2 liters.

If a vessel be divided into two portions by a diaphragm or partition of porous earthenware or dry plaster of Paris, and each half filled with a different gas, diffusion will immediately commence through the pores of the dividing substance, and will continue until perfect mixture has taken place. All gases, however, do not permeate the same porous body, or, in other words, do not pass through narrow orifices, with the same degree of facility. Graham, to whom we are indebted for a very valuable investigation of this interesting subject, established the existence of a very simple relation between the rapidity of diffusion and the density of the gas, which is expressed by saying that the diffusive power varies inversely as the square root of the density of the gas itself. Thus, in the experiment supposed, if one-half of the vessel be filled with hydrogen and the other half with oxygen, the two gases will penetrate the diaphragm at very different rates; four cubic inches of hydrogen will pass into the oxygen side, while one cubic inch of oxygen travels in the opposite direction. The densities of the two gases are to each other in the proportion of 1 to 16; their relative rates of diffusion are inversely as the square roots of these numbers, *i.e.*, as 4 to 1.

In order, however, that this law may be accurately observed, it is necessary that the porous plate be very thin; with plates of stucco an inch thick or more, which really consist of a congeries of long capillary tubes, a different law of diffusion is observed.* An excellent material for diffusion experiments is the artificially compressed graphite of Mr. Brockedon, of the quality used for making writing pencils. It may be reduced by cutting and grinding to the thickness of a wafer, but still retains considerable tenacity. The pores of this substance appear to be so small as entirely to prevent the transmission of gases in mass, so that, to use the language of Mr Graham, it acts like a molecular sieve, allowing only molecules to pass through.

The simplest and most striking method of exhibiting the phenomenon of diffusion is by the use of Graham's diffusion-tube. This is merely a piece of wide glass tube ten or twelve inches long, having one of its extremities closed by a plate of plaster of Paris about half an inch thick, and well dried. When the tube is filled by displacement with hydrogen, and then set upright in a glass of water, the level of the liquid rises in the tube so rapidly, that its movement is apparent to the eye, and speedily attains a height of several inches above the water in the glass. The gas is actually rarefied by its superior diffusive power over that of the external air.

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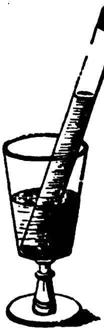
* See Bunsen's Gasometry, p. 203; Graham's Elements of Chemistry, 2d ed. ii. 624; Watts's Dictionary of Chemistry, ii. 815.

Fig. 84



It is impossible to over-estimate the importance in the economy of Nature of this very curious law affecting the constitution of gaseous bodies: it is the principal means by which the atmosphere is preserved in a uniform state, and the accumulation of poisonous gases and exhalations in towns and other confined localities prevented.

A partial separation of gases and vapours of unequal diffusibility may be effected by allowing the mixture to permeate through a plate of graphite or porous earthenware into a vacuum. This effect, called atmolysis, is best exhibited by means of an instrument called the *tube atmolyser*. This is simply a narrow tube of unglazed earthenware, such as a tobacco-pipe stem, two feet long, which is placed within a shorter tube of glass, and secured in its position by corks. The glass tube is connected with an air-pump, and the annular space between the two tubes is made as nearly vacuous as possible. Air or other mixed gas is then allowed to flow along the clay tube in a slow stream, and collected as it issues. The gas or air atmolysed is, of course, reduced in volume, much gas penetrating through the pores of the clay tube into the air-pump vacuum, and the lighter gas diffusing the more rapidly, so that the proportion of the denser constituent is increased in the gas collected. In one experiment, the proportion of oxygen in the air, after traversing the atmolyser, was increased from 20·8 per cent., which is the normal proportion, to 24·5 per cent. With a mixture of oxygen and hydrogen, the separation is, of course, still more considerable.

A distinction must be carefully drawn between real diffusion through small apertures, and the apparently similar passage of gases through membranous diaphragms, such as caoutchouc, bladder, gold-beaters' skin, &c. In this mode of passage, which is called osmose, the rate of interchange depends partly on the relative diffusibilities of the gases, partly on the different degrees of adhesion exerted by the membrane on the different gases, by virtue of which the gas which adheres most powerfully penetrates the diaphragm most easily, and, attaining the opposite surface, mixes with the other. A sheet of caoutchouc tied over the mouth of a wide-mouthed bottle filled with hydrogen, is soon pressed inwards, even to bursting. If the bottle be filled with air, and placed in an atmosphere of hydrogen, the swelling and bursting takes place outwards. If the membrane is moist, the result is likewise affected by the different solubilities of the gases in the water or other liquid which wets it. For example, the diffusive power of carbonic acid into atmospheric air is very small, but it passes into the latter through a wet bladder with the utmost ease, in virtue of its solubility in the water with which the membrane is moistened. It is by such a process that the function of respiration is performed: the aëration of the blood in the lungs, and the disengagement of the carbonic acid, are effected through wet membranes; the blood is never brought into actual contact with the air, but receives its supply of oxygen, and disembarrasses itself of carbonic acid, by this kind of spurious diffusion.

The high diffusive power of hydrogen against air renders it impossible to retain that gas for any length of time in a bladder or caoutchouc bag: it is even unsafe to keep it long in a gas-holder, lest it should become mixed with air by slight accidental leakage, and rendered explosive.

The passage of gases through membranes like caoutchouc or varnished silk, as well as through wet membranes like bladder, appears to depend upon an actual liquefaction of the gases, which then become capable of penetrating the substance of the membrane (as ether and naphtha do), and may again evaporate on the surface and appear as gases. The unequal absorption of gases in this manner often effects a much more complete separation of the components of a gaseous mixture than can be attained by the atmolytic method above described. Thus, Graham has shown that oxygen is absorbed and condensed by caoutchouc two-and-a-half times more abundantly than nitrogen, and that when one side of a caoutchouc film is freely exposed to the air, while a vacuum is produced on the other side, the film allows 41·6 per cent. of oxygen to pass through, instead of the 21 per cent. usually present in the air, so that the air which passes through is capable of rekindling wood burning without flame.

Even metals appear to possess this power of absorbing and liquefying gases. Deville and Troost have observed the remarkable fact that hydrogen gas is capable of penetrating platinum and iron tubes, at a red heat, and Graham is of opinion that this effect may be connected with a power resident in these and certain other metals to absorb and liquefy hydrogen, possibly in its character as a metallic vapour. Platinum in the form of wire or plate, at a low red heat, can take up 3·8 volumes of hydrogen measured cold, and palladium foil condenses as much as 643 times its volume of hydrogen at a temperature below 100° C. In the form of sponge, platinum absorbed 1·48 times its volume of hydrogen, and palladium 90 volumes. This absorption of gases by metals is called occlusion.*

The meteoric iron of Lenarto contains a considerable quantity of occluded hydrogen. When placed in a good vacuum, it yields 2·85 times its volume of gas, of which 85·68 per cent. consist of hydrogen, with 4·46 carbon monoxide and 9·86 nitrogen. Now, hydrogen has been recognised by spectrum analysis in the light of the fixed stars, and constitutes, according to the observations of Father Secchi, the principal element in the atmosphere of a numerous class of stars. "The iron of Lenarto," says Mr. Graham, "has, no doubt, come from such an atmosphere, in which hydrogen greatly prevailed. This meteorite may be looked upon as holding imprisoned within it, and bringing to us, the hydrogen of the stars."*

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* Graham, Phil. Trans. 1866; Journal of the Chemical Society [2], v. 235.

The rates of effusion of gases, that is to say, their rates of passage through a minute aperture in a thin plate of metal or other substance into a vacuum, follow the same law as their rates of diffusion, that is to say, they are inversely as the square roots of the densities of the gases. Nevertheless, the phenomena of diffusion and effusion are essentially different in their nature, the effusive movement affecting masses of a gas, whereas the diffusive movement affects only molecules; and a gas is usually carried by the former kind of impulse with a velocity many thousand times greater than by the latter. Mixed gases are effused at the same rates as one gas of the actual density of the mixture: and no separation of the gases occurs, as in *diffusion* into a vacuum.

The law of effusion just stated is true only under the condition that the gas shall pass through a minute aperture in a very thin plate. If the plate be thicker, so that the aperture becomes a tube, very different rates of efflux are observed; and when the capillary tube becomes considerably elongated, so that its length exceeds its diameter at least 400 times, the rates of flow of different gases into a vacuum again assume a constant ratio to each other, following, however, a law totally distinct from that of effusion. The principal general results observed with relation to this phenomenon of "Capillary Transpiration" are as follows:—

1. The rate of transpiration of the same gas increases, *cæteris paribus* directly as the pressure: in other words, equal volumes of gas at different densities require times inversely proportional to their densities. 2. With tubes of equal diameter, the volume transpired in equal times is inversely as the length of the tube. 3. As the temperature rises, the transpiration of equal volumes becomes slower. 4. The rates of transpiration of different gases bear a constant relation to each other, totally independent of their densities, or, indeed, of any known property of the gases. Equal *weights* of oxygen, nitrogen, and carbon monoxide are transpired in equal times; so likewise are equal weights of nitrogen, nitrogen dioxide, and carbon monoxide; and of hydrogen chloride, carbon dioxide, and nitrogen monoxide.†

COMBINATION OF HYDROGEN WITH OXYGEN.

It has been already stated, that although the light emitted by the flame of pure hydrogen is exceedingly feeble, yet the temperature of the flame is very high. The temperature may be still further exalted by previously mixing the hydrogen with as much oxygen as it requires for combination, that is, as will presently be seen, with half its volume. Such a mixture burns, like gunpowder, independently of the external air. When raised to the temperature required for combination, the two gases unite with explosive violence. If a strong bottle, holding not more than half a pint, be filled with such a mixture, the introduction of a lighted match or red hot wire determines in a moment the union of the gases. By certain precautions, a mixture of oxygen and hydrogen can be burned at a jet without communication of fire to the contents of the vessel; the flame is in this case *solid.*

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* Proceedings of the Royal Society, xv. 502.

† Graham, Phil. Trans. 1846, p. 591, and 1849, p. 349; also Elements of Chemistry, 2d ed. i. 82.

A little consideration will show, that all ordinary flames burning in the air or in pure oxygen are, of necessity, hollow. The act of combustion is nothing more than the energetic union of the substance burned with the surrounding oxygen; and this union can take place only at the surface of the burning body. Such is not the case, however, with the flame now under consideration; the combustible and the oxygen are already mixed, and only require to have their temperature a little raised to cause them to combine in every part. The flame so produced is very different in physical characters from that of a simple jet of hydrogen or any other combustible gas; it is long and pointed, and very remarkable in appearance.

Hemming's safety-jet, the construction of which involves a principle not yet discussed, may be adapted to a common bladder containing the mixture, and held under the arm, and the gas forced through the jet by a little pressure. Although this jet, properly constructed, is believed to be safe, it is best to use nothing stronger than a bladder, for fear of injury in the event of an explosion. The gases are often contained in separate reservoirs, a pair of large gas-holders, for example, and only suffered to mix in the jet itself, as in the contrivance of the late Professor Daniell; in this way all danger is avoided. The eye speedily becomes accustomed to the peculiar appearance of the true oxyhydrogen flame, so as to permit the supply of each gas to be exactly regulated by suitable stop-cocks attached to the jet (fig. 85.)

A piece of thick platinum wire introduced into the flame of the oxyhydrogen blowpipe melts with the greatest ease; a watch-spring or a small steel file burns with the utmost brilliancy, throwing off showers of beautiful sparks; an incombustible oxidised body, as magnesia or lime, becomes so intensely ignited as to glow with a light insupportable to the eye, and to be susceptible of employment as a most powerful illuminator, as a substitute for the sun's rays in the solar microscope, and for night signals in trigonometrical surveys.

If a long glass tube, open at both ends, be held over a jet of hydrogen (fig. 86), a series of musical sounds is sometimes produced by the partial extinction and rekindling of the flame by the ascending current of air. These little explosions succeed each other at regular intervals, and so rapidly as to give rise to a musical note, the pitch depending chiefly upon the length and diameter of the tube.

Fig. 85.

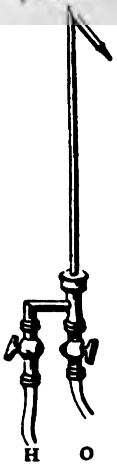
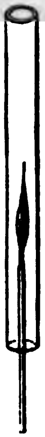


Fig. 86.



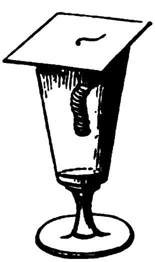
Although oxygen and hydrogen may be kept mixed at common temperatures for any length of time without combination taking place, yet, under particular circumstances, they unite quietly and without explosion. Many years ago, Döbereiner made the curious observation, that finely divided platinum possessed the power of determining the union of the gases; and, more recently, Faraday has shown that the state of minute division is by no means indispensable, since rolled plates of the metal have the same property, provided their surfaces are absolutely clean. Neither is the effect strictly confined to platinum; other metals, as palladium and gold, and even stones and glass, exhibit the same property, although to a far inferior degree, since they often require to be aided by a little heat. When a piece of platinum foil, which has been cleaned by hot oil of vitriol and thorough washing with distilled water, is thrust into a jar containing a mixture of oxygen and hydrogen standing over water, combination of the two gases immediately begins, and the level of the water rapidly rises, whilst the platinum becomes so hot that drops of water accidentally falling upon it enter into ebullition. If the metal be very thin and exceedingly clean, and the gases very pure, its temperature rises after a time to actual redness, and the residue of the mixture explodes. But this is an effect altogether accidental, and dependent upon the high temperature of the platinum, which high temperature has been produced by the preceding quiet combination of the two bodies. When the platinum is reduced to a state of minute division, and its surface thereby much extended, it becomes immediately red-hot in a mixture of hydrogen and oxygen, or hydrogen and air; a jet of hydrogen thrown upon a little of the spongy metal, contained in a glass or capsule, is at once kindled, and on this principle machines for the production of instantaneous light have been constructed. These, however, act well only when constantly used; the spongy platinum is apt to become damp by absorption of moisture from the air, and its power is then for the time lost.

The best explanation that can be given of these curious effects is to suppose that solid bodies in general have, to a greater or less extent, the property of condensing gases upon their surfaces, or even liquefying them (as shown p. 133), and that this faculty is exhibited pre-eminently by certain of the non-oxidisable metals, as platinum and gold. Oxygen and hydrogen may thus, under these circumstances, be brought, as it were, within the sphere of their mutual attractions by a temporary increase of density, whereupon combination ensues.

Coal-gas and ether or alcohol vapour may be made to exhibit the phenomenon of quiet oxidation under the influence of this remarkable surface-action. A close spiral of slender platinum wire, a roll of thin foil, or even a common platinum crucible, heated to dull redness, and then held in a jet of coal-gas, becomes strongly ignited, and remains in that state as long as the supply of mixed gas and air is kept up, the temperature being maintained by the heat disengaged in the act of union. Sometimes the metal becomes white-hot, and then the gas takes fire.

If such a coil of wire be attached to a card, and suspended in a glass containing a few drops of ether, having previously been made red-hot in the flame of a spirit-lamp, it will continue to glow until the oxygen of the air is exhausted, giving rise to the production of an irritating vapour which attacks the eyes. The combustion of the ether is in this case but partial; a portion of its hydrogen is alone removed, and the whole of the carbon left untouched.

Fig. 87.



A coil of thin platinum wire may be placed over the wick of a spirit-lamp, or a ball of spongy platinum sustained just above the cotton; on lighting the lamp, and then blowing it out as soon as the metal appears red-hot, slow combustion of the spirit drawn up by the capillarity of the wick will take place, accompanied by the pungent vapours just mentioned, which may be modified, and even rendered agreeable, by dissolving in the liquid some sweet-smelling essential oil or resin.

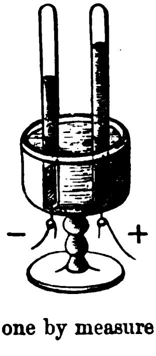
Hydrogen forms numerous compounds with other bodies, although it is greatly surpassed in this respect, not only by oxygen, but by many of the other elements. In many of its chemical relations it resembles the metals, combining with oxygen, sulphur, chlorine, bromine, &c., to form compounds analogous in constitution to the metallic oxides, sulphides, chlorides, bromides, &c. (p. 116).

Oxides of Hydrogen.—There are two oxides of hydrogen—namely, the monoxide, which is water, and the dioxide, discovered in the year 1818 by Thénard.

It appears that the composition of water was first demonstrated in the year 1781 by Cavendish;* but the discovery of the exact proportions in which oxygen and hydrogen unite in generating that most important compound has, from time to time to the present day, occupied the attention of some of the most distinguished cultivators of chemical science. There are two distinct methods of research in chemistry—the *analytical*, or that in which the compound is resolved into its elements, and the *synthetical*, in which the elements are made to unite and produce the compound. The first method is of much more general application than the second; but in this particular instance both may be employed, although the results of the synthesis are the more valuable.

The decomposition of water may be effected by voltaic electricity. When water is acidulated so as to render it a conductor,† and a portion interposed between a pair of platinum plates connected with the extremities of a voltaic apparatus of moderate power, decomposition of the liquid takes place in a very interesting manner; oxygen, in a state of perfect purity, is evolved from the water in contact with the plate belonging to the copper end of the battery, and hydrogen, equally pure, is disengaged at the plate connected with the zinc extremity, the middle portions of liquid remaining apparently unaltered. By placing small graduated jars over the platinum plates, the gases can be collected, and their quantities determined. The whole arrangement is shown in fig. 88; the conducting wires pass through the bottom of the glass cup, and away to the battery.

Fig. 88.



When this experiment has been continued a sufficient time, it will be found that the volume of the hydrogen is a *very* little above twice that of the oxygen. Were it not for the accidental circumstance of oxygen being sensibly more soluble in water than hydrogen, the proportion of two to one by measure would come out exactly.

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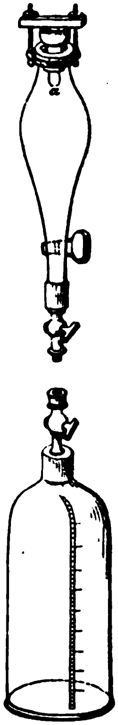
* A claim to the discovery of the composition of water, on behalf of James Watt, has been very strongly urged, and supported by such evidence that the reader of the controversy may be led to the conclusion that the discovery was made by both parties, nearly simultaneously, and unknown to each other. See the article "Gas," by Dr. Paul, in Watts's Dictionary of Chemistry, ii. 780.

† See the section on "Electro-Chemical Decomposition."

Water, as Mr. Grove has shown, is likewise decomposed into its constituents by heat. This effect is produced by introducing platinum balls, ignited by electricity or other means, into water or steam. The two gases are obtained in very small quantities at a time.

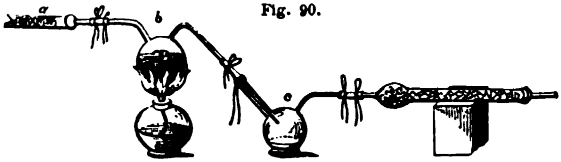
Fig. 89.



When oxygen and hydrogen, both as pure as possible, are mixed in the proportions mentioned, passed into a strong glass tube standing over mercury, and exploded by the electric spark, all the mixture disappears, and the mercury is forced up into the tube, filling it completely. The same experiment may be made with the explosion vessel or eudiometer of Cavendish (fig. 89.) The instrument is exhausted at the air-pump, and then filled from a capped jar with the mixed gases; on passing an electric spark by the wires shown at *a*, explosion ensues, and the glass becomes bedewed with moisture; and if the stop-cock be then opened under water, the latter will rush in and fill the vessel, leaving merely a bubble of air, the result of imperfect exhaustion.

The process upon which most reliance is placed is that in which pure copper oxide is reduced at a red heat by hydrogen, and the water so formed is collected and weighed. This oxide suffers no change by heat alone, but the momentary contact of hydrogen, or any common combustible matter, at a high temperature, suffices to reduce a corresponding portion to the metallic state. Fig. 90 will serve to convey some idea of the arrangement adopted in researches of this kind.

Fig. 90.



A copious supply of hydrogen is procured by the action of dilute sulphuric acid upon the purest zinc that can be obtained; the gas is made to pass in succession through solutions of silver nitrate and strong caustic potash, by which its purification is completed. After this it is conducted through a tube three or four inches long, filled with fragments of pumice-stone steeped in concentrated oil of vitriol, or with anhydrous phosphoric acid. These substances have so great an attraction for aqueous vapour, that they dry the gas completely during its transit. The extremity of this tube is shown at *a*. The dry hydrogen thus arrives at the part of the apparatus containing the copper oxide represented at *b*; this consists of a two-necked flask of very hard white glass, maintained at a red-heat by a spirit-lamp placed beneath. As the decomposition proceeds, the water produced by the reduction of the oxide begins to condense in the second neck of the flask, whence it drops into the receiver *c*. A second desiccating tube prevents the loss of aqueous vapour by the current of gas which passes in excess.

Before the experiment can be commenced, the copper oxide, the purity of which is well ascertained, must be heated to redness for some time in a current of dry air; it is then suffered to cool, and very carefully weighed with the flask. The empty receiver and second drying-tube are also weighed, the disengagement of gas set up, and when the air has been displaced, heat is slowly applied to the oxide. The action is at first very energetic; the oxide often exhibits the appearance of ignition; but as the decomposition proceeds, it becomes more sluggish, and requires the application of a considerable heat to effect its completion.

When the process is at an end, and the apparatus perfectly cool, the stream of gas is discontinued, dry air is drawn through the whole arrangement, and, lastly, the parts are disconnected and reweighed. The loss of the copper oxide gives the oxygen; the gain of the receiver and its drying-tube indicates the water; and the difference between the two, the hydrogen.

A set of experiments, made in Paris in the year 1820, by Dulong and Berzelius, gave as a mean result, for the composition of water by weight, 8·009 parts oxygen to 1 part hydrogen; numbers so nearly in the proportion of 8 to 1, that the latter have usually been assumed to be true.

More recently the subject has been reinvestigated by Dumas, with the most scrupulous precision, and the above supposition fully confirmed. The composition of water may therefore be considered as established; it contains by weight 8 parts oxygen to 1 part hydrogen, and by measure, 1 volume oxygen to 2 volumes hydrogen. The densities of the gases, as already mentioned, correspond very closely with these results.

The physical properties of water are too well known to need lengthened description: when pure, it is colourless and transparent, destitute of taste and odour, and an exceedingly bad conductor of electricity of low tension. It attains its greatest density towards 4·5° C. (40° F.). freezes at 0° C. (32° F.),* and boils under the ordinary atmospheric pressure at or near 100° C. (212° F.). It evaporates at all temperatures.

The weight of a cubic centimeter of water at the maximum density is chosen as the unit of weight of the metrical system; and called a gram; consequently a liter or cubic decimeter = 100 cubic centimeters of water, at the same temperature, weighs 1000 grams, or 1 kilogram.

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* According to Dufour, the specific gravity of ice is 0·9175; water, therefore, on freezing, expands by $\frac{1}{11}$th of its volume.

A cubic inch of water at 62° F. weighs 252·45 grains; a cubic foot weighs nearly 1000 ounces avoirdupois; and an imperial gallon weighs 70,000 grains, or 10 lbs. avoirdupois.

Water is 825 times heavier than air. To all ordinary observation, it is incompressible; very accurate experiments have nevertheless shown that it does yield to a small extent when the power employed is very great, the diminution of volume for each atmosphere of pressure being about 51-millionths of the whole.

Clear water, although colourless in small bulk, is blue like the atmosphere when viewed in mass. This is seen in the deep ultramarine tint of the ocean, and perhaps in a still more beautiful manner in the lakes of Switzerland and other Alpine countries, and in the rivers which issue from them, the slightest admixture of mud or suspended impurity destroying the effect. The same magnificent colour is visible in the fissures and caverns found in the ice of the glaciers, which is usually extremely pure and transparent within, although foul upon the surface.

The specific gravity of steam or vapour of water is found by experiment to be 0·625, compared with air at the same temperature and pressure, or 9 as compared with hydrogen. Now, it has been already shown that water is composed of two volumes of hydrogen and one volume of oxygen; and if the weight of one volume of hydrogen be taken as unity, that of two volumes hydrogen (=2) and one volume oxygen (=16) will together make 18, which is the weight of two volumes of water-vapour. Consequently *water in the state of vapour consists of two volumes of hydrogen and one volume of oxygen condensed into two volumes.* A method of demonstrating this important fact by direct experiment has been devised by Dr. Hofmann. It consists in exploding a mixture of two volumes hydrogen and one volume oxygen, by the electric spark, in a eudiometer tube enclosed in an atmosphere of the vapour of a liquid (amylic alcohol) which boils at a temperature considerably above that of boiling water, so that the water produced by the combination of the gases remains in the state of vapour instead of at once condensing to the liquid form. It is then seen that the three volumes of mixed gas are reduced after the explosion to two volumes.*

Water seldom or never occurs in nature in a state of perfect purity: even the rain which falls in the open country contains a trace of ammoniacal salt, while rivers and springs are invariably contaminated to a greater or less extent with soluble matters, saline and organic. Simple filtration through a porous stone or a bed of sand will separate suspended impurities, but distillation alone will free the liquid from those which are dissolved. In the preparation of distilled water, which is an article of large consumption in the scientific laboratory, it is proper to reject the first portions which pass over, and to avoid carrying the distillation to dryness. The process may be conducted in a metal still furnished with a worm or condenser of silver or tin; lead must not be used.

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* For a description of the apparatus, see Hofmann's Modern Chemistry (1865), p. 51.

The ocean is the great recipient of the saline matter carried down by the rivers which drain the land: hence the vast accumulation of salts. The following table will serve to convey an idea of the ordinary composition of sea-water; the analysis is by Dr Schweitzer, of Brighton, the water being that of the British Channel:—

1000 grains contained—

Water,	964·745
Sodium chloride,	27·059
Potassium chloride,	0·766
Magnesium chloride,	3·666
Magnesium bromide,	0·029
Magnesium sulphate,	2·296
Calcium sulphate,	1·406
Calcium carbonate,	0·033
Traces of Iodine and Ammoniacal salts,	...
	1000·000

Its specific gravity was found to be 1·0274 at 15·5° C. (60° F.). Sea-water is liable to variations of density and composition by the influence of local causes, such as the proximity of large rivers, or masses of melting ice, and other circumstances.

Natural springs are often impregnated to a great extent with soluble substances derived from the rocks they traverse; such are the various mineral waters scattered over the whole earth, and to which medicinal virtues are attributed. Some of these hold ferrous oxide in solution, and are effervescent from carbonic acid gas; others are alkaline, probably from traversing rocks of volcanic origin; some contain a very notable quantity of iodine or bromine. Their temperatures, also, are as variable as their chemical nature.

Water acts on many oxides, both acid and basic, with great energy and considerable evolution of heat, producing compounds called hydroxides, which contain hydrogen and oxygen in the proportion to form water, but not actually existing as water, the elements of the two bodies in combining having undergone a change of arrangement, thus:—

$K_2O + H_2O = 2KHO$ Potassium hydroxide (potash).
$CaO + H_2O = CaH_2O_2$ Calcium hydroxide (slaked lime).
$SO_3 + H_2O = SH_2O_4$ Sulphur hydroxide (sulphuric acid).
$P_2O_5 + H_2O = 2PHO_3$ Phosphorus hydroxide (metaphosphoric acid).

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* Philosophical Magazine, July 1839.

In many of these compounds the elements of water are retained with great force, and require a high temperature to expel them: calcium hydroxide, for example, requires a red heat to convert it into anhydrous calcium oxide (quick lime), and the hydroxides of potassium, barium, sulphur, and phosphorus cannot be dehydrated by heat alone.

In other cases water appears to combine with other bodies—salts, for example—as such, or, in other words, without alteration of atomic arrangement. Such compounds are called hydrates, and the water contained in them—the presence of which has great influence on the crystalline form of the compound—is called water of crystallisation. Water thus combined is easily expelled by heat, mostly at 100–120°.

Many salts combine with different quantities of water, according to the temperature at which they separate from solution, the quantity thus taken up being for the most part greater as the temperature of solidification is lower: thus sodium carbonate crystallises from solution at ordinary temperatures in oblique rhombic prisms containing 10 molecules of water ($CO_3Na_2 + 10H_2O$), whereas at higher temperatures it crystallises as $CO_3Na_2 + 8H_2O$ or $5H_2O$, and from a boiling solution in rectangular plates containing $CO_3Na_2 + H_2O$.

There are also hydrates called cryohydrates,* which exist only at temperatures below the freezing point of water; thus sodium chloride (common salt), which at ordinary temperatures crystallises in anhydrous cubes, solidifies at − 23° with 10½ molecules of water, forming the hydrate $NaCl + 10\frac{1}{2}H_2O$, or $2NaCl + 21H_2O$, and ammonium chloride (sal-ammoniac), also anhydrous at ordinary temperatures, solidifies at −15° to a hydrate containing $NH_4Cl + 12H_2O$.

In some cases water of crystallisation is so feebly combined that it gradually separates when the substance containing it is exposed at ordinary temperatures to dry air, the salt at the same time losing its crystalline character and falling to powder. This change, called efflorescence, is strikingly exhibited by crystallised sodium carbonate and common alum. On the other hand, many substances which are very soluble in water attract water from moist air in such quantity as to form a solution; this change, which is exhibited by calcium chloride and potassium hydroxide (caustic potash), is called deliquescence.

Lastly, the solvent properties of water far exceed those of any other liquid known. Among salts a very large proportion are soluble to a greater or less extent, the solubility usually increasing with the temperature, so that a hot saturated solution deposits crystals on cooling. There are a few exceptions to this law, one of the most remarkable of which is common salt, the solubility of which is nearly the same at all temperatures: the hydroxide and certain organic salts of calcium, also, dissolve more freely in cold than in hot water.

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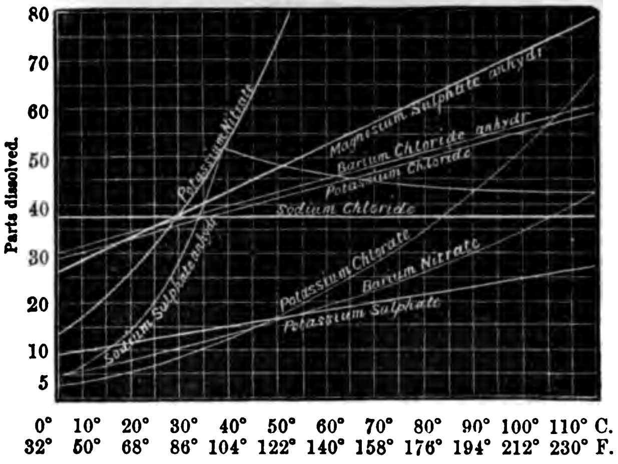
* Guthrie, Phil. Mag. (Ser. 4) xlix. 1, 206; l. 266;—(Ser. 5) i. 49; ii. 211.

Fig. 91 exhibits the unequal solubility of different salts in water of

Solubility of Salts in 100 parts of Water.

Fig. 91.



different temperatures. The *lines of solubility* cut the verticals raised from points indicating the temperatures, upon the lower horizontal line, at heights proportioned to the quantities of salt dissolved by 100 parts of water. The diagram shows, for example, that 100 parts of water dissolve, of potassium sulphate 8 parts at 0° C., 17 parts at 50°, and 25 parts at 100°. There are salts which, like sodium chloride, possess, as already mentioned, very nearly the same degree of solubility in water at all temperatures; in others, like potassium sulphate or potassium chloride, the solubility increases directly with the increment of temperature; in others, again, like potassium nitrate or potassium chlorate, the solubility augments much more rapidly than the temperature. The differences in the deportment of these different salts are shown very conspicuously, by a straight horizontal line, by a straight inclined line, and lastly by curves, the convexity of which is turned towards the lower horizontal line.

The solubility of a salt is usually represented by the quantity of anhydrous salt dissolved by 100 parts of water. It is obvious, however, that salts containing water of hydration or water of crystallisation cannot, within certain limits of temperature, dissolve in water in the anhydrous state, but must be dissolved as hydrates. The solubility of a hydrated salt frequently differs very considerably from that of the same salt in the anhydrous state. Again, many salts, as already observed, form more than one hydrate; and these several hydrates may also differ in their solubility. Sodium sulphate forms a hydrate, $SO_4Na_2+7H_2O$, consisting, in 100 parts, of 53 parts of anhydrous salt and 47 parts of water, which is obtained in crystals, when a solution of sodium sulphate saturated at 100° C., is cooled out of contact with the air: this hydrate is much more soluble than the ordinary hydrate $SO_4Na_2+10H_2O$ (Glauber's salt), which differs from the former in its crystalline form, and consists, in 100 parts, of 44·2 parts of anhydrous salt and 55·8 parts of water. When a solution of sodium sulphate is saturated at the boiling point of water, and cooled to the common temperature without depositing any crystals, the salt exists in the form of the more soluble hydrate. This salt, when coming in contact with the dust of the air, or with a small crystal of common Glauber's salt, is suddenly transformed into the less soluble hydrate, part of which separates from the solution in the form of Glauber's salt. From 0° to 33° C. (32° to 91° F.) sodium sulphate dissolves as Glauber's salt, the solubility of which increases with the temperature: hence the rapid rise of the curve representing the solubility of the salt. Above 33° C. (91° F.) the hydrate of sodium sulphate is decomposed, even in solution, being more and more thoroughly converted into the anhydrous salt as the temperature increases. Sodium sulphate appears, however, far less soluble in the anhydrous state, and hence the diminution of solubility of the salt when its solution is heated above 33° C. (91° F.).

Liquid Diffusion. Dialysis.—When a solution having a sp. gr. greater than water is introduced into a cylindrical glass vessel, and then water very cautiously poured upon it, in such a manner that the two layers of liquid remain unmoved, the substance dissolved in the lower liquid will gradually pass into the supernatant water, though the vessel may have been left undisturbed, and the temperature remain unchanged. This gradual passage of a dissolved substance from its original solution into pure water, taking place notwithstanding the higher specific gravity of the substance which opposes this passage, is called the *diffusion of liquids*. The phenomena of this diffusion have been elaborately investigated by Graham, who has arrived at very important results. Different substances, when in solution of the same concentration, and under other similar circumstances, diffuse with very unequal velocity. Hydrochloric acid, for instance, diffuses with greater rapidity than potassium chloride, potassium chloride more rapidly than sodium chloride, and the latter, again, more quickly than magnesium sulphate; gelatin, albumin, and caramel diffuse very slowly. Diffusion is generally found to take place more rapidly at high than at low temperatures. Diffusion is more particularly rapid with crystallised substances, though not exclusively, for hydrochloric acid and alcohol are among the highly diffusive bodies. Diffusion is slow with non-crystalline bodies, which, like gelatin, are capable of forming a jelly, though even here exceptions are met with. Graham calls the substances of great diffusibility *crystalloïds*, the substances of low diffusibility *colloïds*. The unequal power of diffusion with which different substances are endowed frequently furnishes the means of separating them. When water is poured with caution, so as to prevent mixing, upon a solution containing equal quantities of potassium chloride and sodium chloride, the more diffusible potassium chloride travels more rapidly upwards than the less diffusible sodium chloride, and very considerable portions of potassium chloride will have reached the upper layers of the water before the sodium chloride has arrived there in appreciable quantity. The separation of rapidly diffusible crystalloïds and slowly diffusible colloïds succeeds still better.

A more perfect separation of crystalloïds and colloids may be accomplished in the following manner:—Graham made the important observation, that certain membranes, and also parchment paper, when in contact, on the one surface, with a solution containing a mixture of crystalloïdal and colloïdal substances, and, on the other surface, with pure water, will permit the passage to the water of the crystalloïds, but not of the colloïds. To carry out this important mode of separation, which is designated by the term ***dialysis***, the lower mouth of a glass vessel, open on both sides (fig. 92), is tied over with parchment paper placed upon an appropriate support (fig. 93), and transferred, together with the latter, into a larger vessel filled with water (fig. 94); or the vessel may be suspended, as shown in fig. 95. The liquid containing the different substances in solution is then poured into the inner vessel, so as to form a layer of about half an inch in height upon the parchment

Fig. 92.

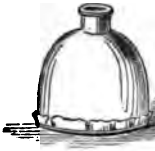


Fig. 93.

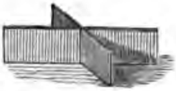


Fig. 94.

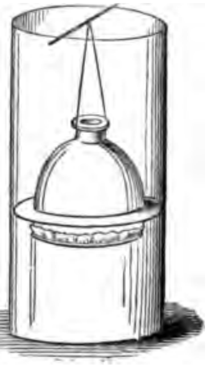
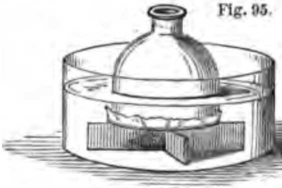


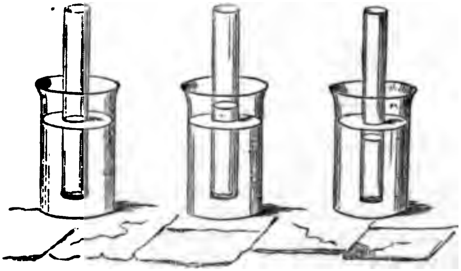
Fig. 95.



paper. The crystalloïdal substances gradually pass through the parchment paper into the outer water, which may be renewed from time to time; the colloïdal substances are almost entirely retained by the liquid in the inner vessel. In this manner Graham prepared several colloïds free from crystalloïds; he showed, moreover, that poisonous crystalloïds, such as arsenious acid or strychnine, even when mixed with very large proportions of colloïdal substances, pass over into the water of the dialyser in such a state of purity that their presence may be established by re-agents with the utmost facility.

Osmose.—When two different liquids are separated by a porous diaphragm, as, for instance, by a membrane, and the liquids mix through this diaphragm, it is found that in most cases the quantities travelling in opposite directions are unequal. Suppose three cylinders, the lower mouths of which are tied over with bladders filled respectively with concentrated solutions of copper sulphate, sodium chloride, and alcohol, and let them be immersed in vessels containing water, to such a depth that the liquids inside and outside are level (fig. 96). After some time the liquid within the tube is found to have risen appreciably above the level of the water (fig. 97). On the other hand, if the cylinder filled with pure water be immersed in a solution of copper sulphate, or of sodium chloride, or in alcohol, the liquid in the cylinder is seen to diminish after some time (fig. 98). A larger quantity of water passes through the bladder into the solution of copper sulphate, of sodium chloride, or into alcohol, than the amount of either of these three liquids which passes through the bladder into the water. The mixing of dissimilar substances through a porous diaphragm is called *osmose*. The passage in larger proportions of one liquid into another is designated by the term *exosmose*.

Fig. 96. Fig. 97. Fig. 98.



These phenomena are due to the attraction which the two liquids have for each other, and to the difference of the attraction exercised by the diaphragm upon these liquids. Bladder takes up a much larger quantity of water than of a solution of salt or of alcohol. Very rarely only one of the liquids traverses the diaphragm;

generally two currents of unequal strength move in opposite directions. When water is separated by an animal membrane from a solution of salt or from alcohol, not only is a transition of water to these liquids observed, but a small quantity of hydrochloric acid and of alcohol also passes over into the water. In some cases, however, when colloïdal substances in concentrated solutions are on one side of the diaphragm and water on the other, the latter alone traverses the diaphragm, not a trace of the former passing through to the water.

Water likewise dissolves gases. Solution of gases in water (or in other liquids) is called *absorption*, unless this solution gives rise to the formation of chemical compounds in definite proportions. The phenomena of absorption have been more particularly studied by Bunsen, to whom we are indebted for the most accurate examination of this subject.

Water dissolves very unequal quantities of the different gases, and very unequal quantities of the same gas at different temperatures. 1 vol. of water absorbs, at the temperatures stated in the table, and under the pressure of 30 inches of mercury, the following volumes of different gases, measured at 0° C. and 30 inches pressure :—

	Oxygen.	Nitrogen.	Hydrogen.	Nitrogen Monoxide.	Carbon Dioxide.
0° C. . .	0·041	0·020	0·019	1·31	1·80
10° . .	0·033	0·016	0·019	0·92	1·18
20° . .	0·028	0·014	0·019	0·67	0·90

	Chlorine.	Hydrogen Sulphide.	Sulphurous Oxide.	Hydrochloric Acid.	Ammonia.
0° C. . .	—	4·37	53·9	505	1180
10° . .	2·59	3·59	36·4	472	898
20° . .	2·16	2·91	27·3	441	680
30° . .	1·75	2·33	20·4	412	536
40° . .	1·37	1·86	15·6	387	444

When the pressure increases, a larger quantity of the gases is absorbed. Gases moderately soluble in water follow in their solubility the law of Henry and Dalton, according to which the quantity of gas dissolved is proportional to the pressure. At 10° C. 1 vol. of water absorbs, under a pressure of 1 atmosphere, 1·18 vol. of carbon dioxide, measured at 0° and under a pressure of 30 inches mercury. The quantity of carbon dioxide dissolved under a pressure of 2 atmospheres, and measured under conditions precisely similar to those of the previous experiments, equals 2·36 vols. Again, 1 vol. of water dissolves under a pressure of ½ atmosphere, 0·59 vol. of carbon dioxide also measured at 0° and under 30 inches of mercury. Gases which are exceedingly soluble in water do not obey this law, except at higher temperatures, when the solubility has been already considerably diminished.

It deserves, however, to be noticed, that the pressure which determines the rate of absorption of a gas is by no means the general pressure to which the absorbing liquid is exposed, but that pressure which the gas under consideration would exert if it were alone present in the space with which the absorbing liquid is in contact. Thus, supposing water to be in contact with a mixture of 1 vol. of carbon dioxide and 3 vols. of nitrogen, under a pressure of 4 atmospheres, the amount of carbon dioxide dissolved by the water will be by no means equal to that which the water would have absorbed if it had been, at the same pressure of 4 atmospheres, in contact with pure carbon dioxide. In a mixture of carbon dioxide and nitrogen in the stated proportions, the carbon dioxide exercises only $\frac{1}{4}$, the nitrogen only $\frac{3}{4}$, of the total pressure of the gaseous mixture (4 atmospheres); the partial pressure due to the carbon dioxide is in this case 1 atmosphere, that due to the nitrogen 3 atmospheres; and water, though exposed to a pressure of 4 atmospheres, cannot, under these circumstances, absorb more carbon dioxide than it would if it were in contact with pure carbon dioxide under a pressure of 1 atmosphere.

It is necessary to bear this in mind in order to understand why the air which is absorbed by water out of the atmosphere differs in composition from atmospheric air. The latter consists very nearly of 21 vols. of oxygen and 79 vols. of nitrogen. In atmospheric air which acts under a pressure of 1 atmosphere, the oxygen exerts a partial pressure of $\frac{21}{100}$, the nitrogen a partial pressure of $\frac{79}{100}$ atmosphere. At 10° C. 1 vol. of water (see the above table) absorbs 0·033 vol. of oxygen and 0·016 vol. of nitrogen, supposing these gases to act in the pure state under a pressure of 1 atmosphere. But under the partial pressures just indicated, water of 10° C. cannot absorb more than $\frac{21}{100} \times 0·033 = 0·007$ of oxygen, and $\frac{79}{100} \times 0·016 = 0·13$ vol. of nitrogen. In $0·007 + 0·13 = 0·020$ vol. of the gaseous mixture absorbed by water there are consequently 0·007 vol. of oxygen, and 0·013 vol. of nitrogen, or in 20 vols. of this mixture, 7 vols. of oxygen, and 13 vols. of nitrogen, or in 100 vols. of the gaseous mixture, 35 vols. of oxygen and 69 vols. of nitrogen. The air contained at the common temperature in water is thus seen to be very much richer in oxygen than ordinary atmospheric air. This property of water to absorb oxygen from the air more readily than nitrogen has been applied to the preparation of oxygen for industrial use.*

Air is pressed into water by means of a forcing-pump, and the gases which escape on diminishing the pressure are subjected to the same treatment eight times in succession, by which time nearly pure oxygen is obtained. The following table shows the composition of the gaseous mixture at each successive stage:—

Atmospheric air.		Composition after successive pressures.							
		1	2	3	4	5	6	7	8
N . .	79	66·67	52·5	37·5	25·0	15·0	9·0	5·0	2·7
O . .	21	33·33	47·5	62·5	75·0	85·0	91·0	95·0	97·3

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* Mallet, Dingler's Polyt. Journal, cxcix. 112.

Water containing a gas in solution, when exposed in a vacuum or in a space filled with another gas, allows the gas absorbed to escape until the quantity retained corresponds with the share of the pressure belonging to the gas evolved. If the latter be constantly removed by a powerful absorbent or by a good air-pump, it is in most cases easy to separate every trace of gas from the water. The same result is obtained when water containing a gas in solution is exposed in a space of comparatively infinite size filled with another gas. Water in which nitrogen monoxide is dissolved loses the latter entirely by mere exposure to the atmosphere, and the gas evolved cannot, at any moment, exert more than an infinitely small share of the pressure. If water be freed from gases by ebullition, the separation depends partly upon the diminution of the solubility by the increase of temperature, partly also upon the formation above the surface of the liquid of a constantly renewed atmosphere into which the gas still retained by the liquid may escape.

Some gases which are absorbed in large quantities, and very quickly by water—hydrochloric acid, for instance—cannot be perfectly expelled either by the protracted action of another gas (exposure to the atmosphere) or by ebullition; in such cases the liquid, still charged with gas, evaporates as a whole when it has assumed a certain composition. This composition varies, however, with the temperature if the liquid be submitted to a current of air, and with the pressure if it be boiled.

Liquids also lose the gas they contain in solution by freezing: hence the air-bubbles in ice, which consist of the air which had been absorbed from the atmosphere by the water. Gas is retained by liquids at the freezing temperature only when it forms a chemical combination in definite proportion with the liquid. Water containing chlorine or sulphurous acid in solution freezes without evolution of gas, with formation of a solid hydrate of chlorine or sulphurous acid.

Pure water generally dissolves gases more copiously than water containing solid bodies in solution (salt water, for instance). If in some few cases exceptions are observed to take place, they appear to depend upon the formation of feeble but true chemical compounds in definite proportion; the fact that carbon dioxide is more copiously absorbed by water containing sodium phosphate in solution than by pure water, may perhaps be explained in this manner.

When water is heated in a strong vessel to a temperature above that of the ordinary boiling point, its solvent powers are still further increased. Dr. Turner enclosed in the upper part of a high-pressure steam-boiler, worked at 149° C. (300° F.), pieces of plate and crown glass. At the expiration of four months the glass was found completely corroded by the action of the water; what remained was a white mass of silica, destitute of alkali, while stalactites of siliceous matter, above an inch in length, depended from the little wire cage which enclosed the glass. This experiment tends to illustrate the changes which may be produced by the action of water at a high temperature in the interior of the earth upon felspathic and other rocks. The phenomenon is manifest in the Geyser springs of Iceland, which deposit siliceous sinter.

Hydrogen Dioxide, H_2O_2, sometimes called *Oxygenated water*, is an exceedingly interesting substance, but very difficult of preparation. It is formed by dissolving barium dioxide in dilute hydrochloric acid carefully cooled by ice, and then precipitating the barium by sulphuric acid; the excess of oxygen of the dioxide, instead of being disengaged as gas, unites with a portion of the water, and converts it into hydrogen dioxide. This treatment is repeated with the same solution and fresh portions of the barium dioxide, until a considerable quantity of the latter has been consumed, and a corresponding amount of hydrogen dioxide formed. The liquid yet contains hydrochloric acid, to get rid of which it is treated in succession with silver sulphate and baryta-water. The whole process requires the utmost care and attention. The barium dioxide itself is prepared by exposing pure baryta, contained in a red-hot porcelain tube, to a stream of oxygen. The solution of hydrogen dioxide may be concentrated under the air-pump receiver until it acquires the specific gravity of 1·45. In this state it presents the aspect of a colourless, transparent inodorous liquid, possessing remarkable bleaching powers. It is very prone to decomposition; the least elevation of temperature causes effervescence, due to the escape of oxygen gas; near 100° it is decomposed with explosive violence. Hydrogen dioxide contains exactly twice as much oxygen as water, or 16 parts to one part of hydrogen.

NITROGEN.

Atomic weight, 14; symbol, N.

NITROGEN* constitutes about four-fifths of the atmosphere, and enters into a great variety of combinations. It may be prepared by several methods. One of the simplest of these is to burn out the oxygen from a confined portion of air by phosphorus, or by a jet of hydrogen.

A small porcelain capsule is floated on the water of the pneumatic trough, and a piece of phosphorus is placed in it and set on fire. A bell-jar is then inverted over the whole, and suffered to rest on the shelf of the trough, so as to project a little over its edge. At first the heat causes expansion of the air of the jar, and a few bubbles are expelled, after which the level of the water rises considerably. When the phosphorus becomes extinguished by exhaustion of the oxygen, and time has been given for the subsidence of the cloud of finely divided snow-like phosphoric oxide which floats in the residual gas, the nitrogen may be transferred into another vessel, and its properties examined.

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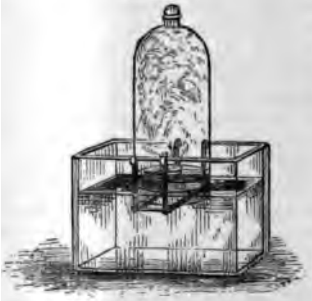
* *i.e.*, Generator of nitre; also called *Azote*, from *a*, privative, and ζωή, life.

Fig. 99.



Prepared by the foregoing process, nitrogen is contaminated with a little vapour of phosphorus, which communicates its peculiar odour. A preferable method is to fill a porcelain tube with turnings of copper, or, still better, with the spongy metal obtained by reducing the oxide with hydrogen; to heat this tube to redness; and then pass through it a slow stream of atmospheric air, the oxygen of which is entirely removed, during its progress, by the heated copper.

If chlorine gas be passed into solution of ammonia, the latter substance, which is a compound of nitrogen with hydrogen, is decomposed; the chlorine combines with the hydrogen, and the nitrogen is set free, with effervescence. In this manner very pure nitrogen can be obtained. In making this experiment, it is necessary to stop short of saturating or decomposing the whole of the ammonia; otherwise there will be great risk of accident from the formation of an exceedingly dangerous explosive compound, produced by the contact of chlorine with an ammoniacal salt.

Another very easy and perfectly safe method of obtaining pure nitrogen is to decompose a solution of potassium nitrite with ammonium chloride (sal-ammoniac). The potassium nitrite is prepared by passing the red vapours of nitrous acid, obtained by heating dilute nitric acid with starch, into a solution of caustic potash. On boiling the resulting solution with sal-ammoniac, nitrogen gas is evolved, while potassium chloride remains in solution. The reaction is represented by the equation,

$$\underset{\substack{\text{Potassium}\\\text{nitrite.}}}{KNO_2} + \underset{\substack{\text{Ammonium}\\\text{chloride.}}}{NH_4Cl} = \underset{\substack{\text{Potassium}\\\text{chloride.}}}{KCl} + \underset{\text{Water.}}{2H_2O} + \underset{\substack{\text{Nitrogen}\\\text{gas.}}}{N_2}.$$

Nitrogen is destitute of colour, taste, and odour; it is a little lighter than air, its density being 0·972. A liter of the gas at 0° C. and 760 mm. barometric pressure weighs 1·25658 gram. 100 cubic inches, at 60° F. and 30 inches barometer, weigh 30·14 grains. Nitrogen is incapable of sustaining combustion or animal life, although, like hydrogen, it has no positive poisonous properties; neither is it soluble to any notable extent in water or in caustic alkali; it is, in fact, best characterised by negative properties.

Atmospheric Air.—The exact composition of the atmosphere has repeatedly been made the subject of experimental research. Besides nitrogen and oxygen the air contains a little carbon dioxide (carbonic acid), a very variable proportion of aqueous vapour, a trace of ammonia, and, perhaps, a little carburetted hydrogen. The oxygen and nitrogen are in a state of mixture, not of combination, yet their ratio is always uniform. Air has been brought from lofty Alpine heights, and compared with that from the plains of Egypt; it has been brought from an elevation of 21,000 feet by the aid of a balloon; it has been collected and examined in London and Paris, and many other places; still the proportion of oxygen and nitrogen remains unaltered, the diffusive energy of the gases being adequate to maintain this perfect uniformity of mixture. The carbon dioxide, on the contrary, being much influenced by local causes, varies considerably. In the following table the proportions of oxygen and nitrogen are given on the authority of Dumas, and the carbon dioxide on that of De Saussure: the ammonia, the discovery of which in atmospheric air is due to Liebig, is too small in quantity for direct estimation.

Composition of the Atmosphere.

	By weight.	By measure.
Nitrogen, ...	77 parts	79·19
Oxygen, ...	23 „	20·81
	100	100·00

Carbon dioxide, from 3·7 measures to 6·2 measures in 10,000 measures of air.

Aqueous vapour variable, depending much upon the temperature.

Ammonia, a trace.

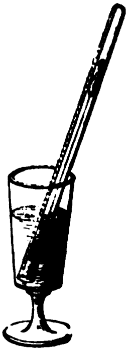
Dr. Frankland has analysed samples of air taken by himself in the valley of Chamouni, on the summit of Mont Blanc, and at the Grands Mulets. The following are the results of his analyses:—

	Carbon Dioxide.	Oxygen.
Chamouni (3000 feet), . .	0·063	20·894
Grands Mulets (11,000 feet), .	0·111	20·802
Mont Blanc (15,732 feet), .	0·061	20·963

A liter of pure and dry air at 0° C. and 760 mm. pressure weighs 1·29366 grams. 100 cubic inches at 60° F. and 30 inches barom. weigh 30·935 grains: hence a cubic foot weighs 536·96 grains, which is $\frac{1}{815}$ of the weight of a cubic foot of water at the same temperature.

The analysis of air is very well effected by passing it over finely divided copper contained in a tube of hard glass, carefully weighed and then heated to redness: the nitrogen is suffered to flow into an exhausted glass globe, also previously weighed. The increase in weight of the copper after the experiment gives the amount of oxygen, and the increase in weight of the exhausted globe gives the nitrogen.

Fig. 100.

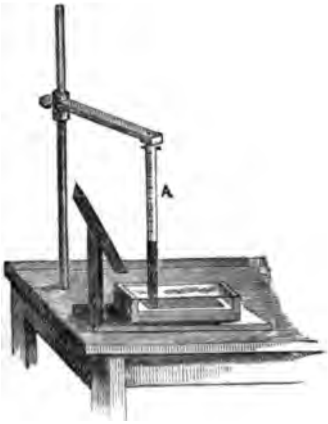


An easier, but less accurate method, consists in introducing into a graduated tube, standing over water, a known quantity of the air to be examined, and then passing into the latter a stick of phosphorus affixed to the end of a wire. The whole is left about twenty-four hours, during which the oxygen is slowly but completely absorbed, after which the phosphorus is withdrawn, and the residual gas read off.

Liebig proposed the use of an alkaline solution of pyrogallic acid (a substance which will be described in the department of organic chemistry) for the absorption of oxygen. The absorptive power of such a solution, which turns deep black on coming in contact with the oxygen, is very considerable. Liebig's method combines great accuracy with unusual rapidity and facility of execution.

Another plan is to mix the air with hydrogen and pass an electric spark through the mixture: after explosion the volume of gas is read off and compared with that of the air employed. Since the analysis of gaseous bodies by explosion is an operation of great importance, it may be worth while to describe the process in detail, as it is applicable, with certain obvious variations, to a number of analogous cases.

Fig. 101.



Instruments for this purpose are called **eudiometers**. The simplest, and, on the whole, the most convenient, consists of a straight graduated glass tube (fig. 101) closed at the top, and having platinum wires inserted near the closed end, to give passage to an electric spark. This tube is filled with mercury, and inverted in a mercurial pneumatic trough.

For the analysis of air, a quantity sufficient to fill about one-sixth of the tube is introduced, and its volume accurately ascertained by reading off with a telescope the number of divisions on the tube to which the mercury reaches, whilst the height of the column of mercury in the tube above the trough, together with that of the barometer, and the temperature of the air, are also read off. A quantity of pure hydrogen gas is now added, more than sufficient to unite with all the oxygen present (about half the volume of the air); and the volume of the gas and the pressure exerted upon it, are determined as before. An electric spark isnow passed through the mixture, care being taken to prevent any escape, by pressing the open end of the eudiometer against a piece of sheet caoutchouc under the mercury in the trough. After the explosion, the volume is again determined, and is found to be less than that before the explosion. The volume of gas read off must in each case be reduced to standard pressure and temperature by the method already given (p. 30).

Now, since the hydrogen is in excess, and 2 volumes of that gas unite with 1 volume of oxygen to form water, one-third of the diminution must be the volume of the oxygen contained in the air introduced. An example will render this clear:—

Air introduced, ...	100 measures.
Air and hydrogen, ...	160
Volume after explosion, . . .	97
Diminution, ...	63

$$\frac{63}{3} = 21 = \text{oxygen in the 100 measures.}$$

Compounds of Nitrogen and Oxygen.

There are five distinct compounds of nitrogen and oxygen, thus named and constituted:—

		Composition.			
		By weight		By volume.	
	Formula.	Nitrogen.	Oxygen.	Nitrogen.	Oxygen.
Monoxide, . . .	N_2O	28	16	2	1
Dioxide, . . .	N_2O_2 or NO	28	32	2	2
Trioxide, or Nitrous oxide, . . .	N_2O_3	28	48	2	3
Tetroxide, . . .	N_2O_4 or NO_2	28	64	2	4
Pentoxide, or Nitric oxide, . . .	N_2O_5	28	80	2	5

A comparison of these numbers will show that the quantities of oxygen which unite with a given quantity of nitrogen are to one another in the ratio of the numbers 1, 2, 3, 4, 5.

The first, third, and fifth of the compounds in the table are capable of taking up the elements of water and of metallic oxides to form salts (p. 123), called respectively hyponitrites, nitrites, and nitrates, the hydrogen salts being also called hyponitrous, nitrous, and nitric acid.

The composition of these acids and of their potassium salts is represented by the following formulæ:—

Hydrogen hyponitrite, or Hyponitrous acid,	$H_2O.N_2O$	or HNO
Potassium hyponitrite, ...	$K_2O.N_2O$	or KNO
Hydrogen nitrite, or Nitrous acid, .	$H_2O.N_2O_3$	or HNO_2
Potassium nitrite, ...	$K_2O.N_2O_3$	or KNO_2
Hydrogen nitrate, or Nitric acid, .	$H_2O.N_2O_5$	or HNO_3
Potassium nitrate, ...	$K_2O.N_2O_5$	or KNO_3

The dioxide and tetroxide of nitrogen do not form salts.

It will be convenient to commence the description of these compounds with the last on the list, viz., the pentoxide, as its salts, the nitrates, are the sources from which all the other compounds in the series are obtained.

Nitrogen Pentoxide, or Nitric Oxide, N_2O_5. (also called *Anhydrous Nitric Acid*, or *Nitric Anhydride.*)—This compound was discovered in 1849 by Deville, who obtained it by exposing silver nitrate to the action of chlorine gas. Chlorine and silver then combine, forming silver chloride, which remains in the apparatus, while oxygen and nitrogen pentoxide separate:

$$Ag_2O.N_2O_5 + Cl_2 = 2AgCl + N_2O_5.$$

It may also be prepared by slowly distilling pure and highly concentrated nitric acid at a blood-heat with phosphoric oxide, a substance which has a very powerful attraction for water. The distillate consists of two layers of liquid, the upper of which is nitrogen pentoxide mixed with nitrous and nitric acids; and on separating this upper layer, and cooling it with ice or a freezing mixture, the pentoxide separates in crystals.

Nitrogen pentoxide is a colourless substance, crystallising in six-sided prisms, which melt at 30°, and boil between 45° and 50°, when they begin to decompose. Its specific gravity in the solid state as above 1·64; in the liquid state below 1·636. Nitrogen pentoxide sometimes explodes spontaneously. It dissolves in water with great rise of temperature, forming hydrogen nitrate or nitric acid. It also unites with a smaller proportion of water, forming the *hemihydrate* $2N_2O_5.H_2O$, which constitutes the chief part of the lower layer of the distillate obtained in the manner just described. It is liquid at ordinary temperatures, but crystallises in a freezing mixture.

NITRATES—NITRIC ACID.—In certain parts of India, and in other hot dry climates where rain is rare, the surface of the soil is occasionally covered by a saline efflorescence, like that sometimes apparent on newly plastered walls; this substance collected, dissolved in hot water, and crystallised from the filtered solution, furnishes the highly important salt known in commerce as nitre or saltpetre, and consisting of potassium nitrate. To obtain nitric acid, equal weights of powdered nitre and strong sulphuric acid are introduced into a glass retort, and heat is applied by means of a gas-lamp or charcoal chauffer. A flask, cooled by a wet cloth, is adapted to the retort to serve for a receiver. No luting of any kind must be used.

As the distillation advances, the red fumes which first arise disappear, but towards the end of the process they again become manifest. When this happens, and very little liquid passes over, while the greater part of the saline matter of the retort is in a state of tranquil fusion, the operation may be stopped; and when the retort is quite cold, water may be introduced to dissolve out the saline residue. The reaction consists in an interchange between the potassium of the nitre and half the hydrogen of the sulphuric acid (hydrogen sulphate), whereby there are formed hydrogen nitrate which distils over, and hydrogen and potassium sulphate which remains in the retort.

$$\underset{\substack{\text{Potassium}\\\text{nitrate.}}}{KNO_3} + \underset{\substack{\text{Hydrogen}\\\text{sulphate.}}}{H_2SO_4} = \underset{\substack{\text{Hydrogen}\\\text{nitrate.}}}{HNO_3} + \underset{\substack{\text{Hydrogen and}\\\text{potassium sulphate.}}}{HKSO_4}$$

In the manufacture of nitric acid on the large scale, the glass retort is replaced by a cast-iron cylinder, and the receiver by a series of earthen condensing vessels connected by tubes. Sodium nitrate, found native in Peru, is now generally substituted for potassium nitrate.

Nitric acid thus obtained has a specific gravity of from 1·5 to 1·52; it has a golden-yellow colour, due to nitrogen trioxide, or tetroxide, which is held in solution, and, when the acid is diluted with water, gives rise by its decomposition to a disengagement of nitrogen dioxide. Nitric acid is exceedingly corrosive, staining the skin deep yellow, and causing total disorganisation. Poured upon red-hot powdered charcoal, it causes brilliant combustion; and when added to warm oil of turpentine, acts upon that substance so energetically as to set it on fire.

Pure nitric acid, in its most concentrated form, is obtained by mixing the above with about an equal quantity of strong sulphuric acid, redistilling, collecting apart the first portion which comes over, and exposing it, in a vessel slightly warmed and sheltered from the light, to a current of dry air made to bubble through it, which completely removes the nitrous acid. In this state the product is as colourless as water; it has the sp. gr. 1·517 at 15·5° (60° F.), boils at 84·5° (184° F.), and consists of 54 parts nitrogen pentoxide and 9 parts water. Although nitric acid in a more dilute form acts very violently upon many metals, and upon organic substances generally, this is not the case with the most concentrated acid: even at a boiling heat, it refuses to attack iron or tin; and its mode of action on lignin, starch, and similar substances, is quite peculiar, and very much less energetic than that of an acid containing more water.

On boiling nitric acid of different degrees of concentration, at the ordinary atmospheric pressure, a residue is left, boiling at 120·5° and 29 inches barometer, and having the sp. gr. 1·414 at 15·5°. This acid was formerly supposed to be a definite compound of nitric acid with water; but Roscoe has recently proved this assumption to be incorrect, the composition of the acid varying according to the pressure under which the liquid boils.

The nitrates form a very extensive and important group of salts, which are remarkable for being all soluble in water. Hydrogen nitrate is of great use in the laboratory, and in many branches of industry.

The acid prepared in the way described is apt to contain traces of chlorine from common salt in the nitre, and sometimes of sulphate from accidental splashing of the pasty mass in the retort. To discover these impurities, a portion is diluted with four or five times its bulk of distilled water, and divided between two glasses. Solution of silver nitrate is dropped into the one, and solution of barium nitrate into the other; if no change ensue in either case, the acid is free from the impurities mentioned.

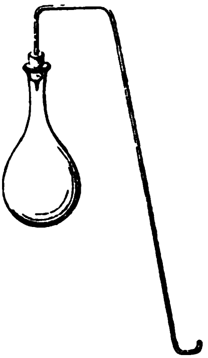
Nitric acid has been formed in small quantity, by passing a series of electric sparks through a portion of air in contact with water or an alkaline solution. The amount of acid so formed after many hours is very minute; still it is not impossible that powerful discharges of atmospheric electricity may sometimes occasion a trifling production of nitric acid in the air. A very minute quantity of nitric acid is produced by the combustion of hydrogen and other substances in the atmosphere; it is also formed by the oxidation of ammonia.

Nitric acid is not so easily detected in solution in small quantities as many other acids. Owing to the solubility of all its compounds, no *precipitant* can be found for this acid. A good mode of testing it is based upon its power of bleaching a solution of indigo in sulphuric acid when boiled with that liquid. The absence of chlorine must be insured in this experiment by means which will hereafter be described; otherwise the result is equivocal.

The best method for the detection of nitric acid is the following: —The substance to be examined is boiled with a small quantity of water, and the solution cautiously mixed with an equal volume of concentrated sulphuric acid; the liquid is then allowed to cool, and a strong solution of ferrous sulphate carefully poured upon it, so as to form a separate layer. If large quantities of nitric acid are present, the surface of contact first, and then the whole of the liquid, becomes black. If but small quantities of nitric acid are present, the liquid becomes reddish-brown or purple. The ferrous sulphate reduces the nitric acid to nitrogen dioxide, which, dissolving in the solution of ferrous sulphate, imparts to it a dark colour.

Nitrogen Monoxide, N_2O (sometimes called *Nitrous Oxide; also Laughing Gas.*)—When solid ammonium nitrate is heated in a retort or flask[*] (fig. 102), furnished with a perforated cork and bent tube, it is resolved into water and nitrogen monoxide, $NH_4NO_3 = 2H_2O + N_2O$.

Fig. 102.



No particular precaution is required in the operation, save due regulation of the heat, and the avoidance of tumultuous disengagement of the gas.

Nitrogen monoxide is a colourless, transparent, and almost inodorous gas, of distinctly sweet taste. Its specific gravity is 1·525; a litre of it weighs 1·97172 gram; 100 cubic inches weigh 47·29 grains. It supports the combustion of a taper or a piece of phosphorus with almost as much energy as pure oxygen: it is easily distinguished, however, from that gas by its solubility in cold water, which dissolves nearly its own volume: hence it is necessary to use tepid water in the pneumatic trough or gas-holder, otherwise great loss of gas will ensue.

Gaseous nitrogen monoxide mixed with an equal volume of hydrogen, and fired by the electric spark in the eudiometer, explodes with violence, and liberates its own measure of nitrogen. Every two volumes of the gas must consequently contain two volumes of nitrogen and one volume of oxygen, the whole condensed or contracted one-third—a constitution resembling that of vapour of water.

The most remarkable property of this gas is its intoxicating power upon the animal system. If quite pure, or merely mixed with atmospheric air, it may be respired for a short time without danger or inconvenience. The effect is very transient, and is not followed by depression. The gas is now much used as an anæsthetic in dental surgery.

Nitrogen monoxide has been liquefied, but with difficulty; it requires, at 45° F. (7·2°C.), a pressure of 50 atmospheres: the liquid monoxide has a specific gravity of 0·9004; it is not miscible with water. Faraday solidified it by exposing it in a sealed tube to the cold produced by a mixture of solid carbonic acid and ether, but he supposed that it could not be solidified by the cold produced by its own evaporation. This, however, may be effected if the evaporation be accelerated by a strong current of air. A very fine steel tube is directed into the axis of a thin brass cone, having a small opening, about the eighth of an inch, at its apex. On causing a stream of the liquid to issue from the jet, it is retained in the cone for a moment, and then forcibly blown out at the apex, together with a strong stream of air. The solid is in this way formed in some quantity, and may be collected in a dish lined with filter-paper, or other suitable vessel. Solid nitrogen monoxide is more compact in appearance than solid carbonic acid, and, unlike the latter, it melts and boils, if gently warmed, before passing into the gaseous state: hence if placed in contact with the skin, it produces a painful blister, like a burn. The melting or freezing point of the monoxide is −120° F. or −99° C., and its boiling point −109° F. or −92° C. It is the proximity of the boiling and freezing points which renders it possible to freeze the liquid by simply blowing air through it.*

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[*] Florence oil-flasks, which may be purchased at a very trifling sum, constitute exceedingly useful vessels for chemical purposes, and often supersede retorts or other expensive apparatus. They are rendered still more valuable by cutting the neck smoothly round with a hot iron, softening it in the flame of a good Argand gas-lamp, or Bunsen burner, and then turning over the edge so as to form a lip or border. The neck will then bear a tightly-fitting cork without risk of splitting.

HYPONITROUS ACID, $N_2O.H_2O$, or HNO.—When a solution of sodium nitrate, $NaNO_3$, or ammonium nitrate, $NH_4.NO_3$, is treated with sodium amalgam (a compound of sodium and mercury), the nitrate gives up 2 atoms of oxygen to the sodium, and is reduced to hyponitrite, NaNO. On neutralising the excess of alkali in the liquid, by adding acetic acid till the solution no longer gives a brown or black precipitate (of silver oxide) with silver nitrate, a solution of sodium hyponitrite is obtained, which is alkaline to test-paper, and gives with silver nitrate a yellow precipitate of silver hyponitrite, AgNO. When the original alkaline liquid is acidified with acetic acid, and heated, the hyponitrous acid is resolved into water and nitrogen monoxide, which escapes as gas, $2HNO = H_2O + N_2O$.†

Nitrogen Dioxide, N_2O_2 or NO (sometimes called *Nitric Oxide.*)—Clippings or turnings of copper are put into the apparatus employed for preparing hydrogen (p. 129), together with a little water, and nitric acid is added by the funnel until brisk effervescence is excited. The gas may be collected over cold water, as it is not sensibly soluble.

The reaction is a simple deoxidation of some of the nitric acid by the copper: the metal is oxidised, and the oxide so formed is dissolved by another portion of the acid, forming copper nitrate. Nitric acid is very prone to act thus upon certain metals:—

$$\underset{\text{Nitric Acid.}}{8HNO_3} + Cu_3 = N_2O_2 + \underset{\text{Copper nitrate.}}{3Cu(NO_3)_2} + 4H_2O.$$

The gas obtained in this manner is colourless and transparent: in contact with air or oxygen gas it produces deep red fumes, which are readily absorbed by water: this character is sufficient to distinguish it from all other gaseous bodies. A lighted taper plunged into the gas is extinguished; lighted phosphorus, however, burns in it with great brilliancy.

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* Wills, Chem. Soc. Jour. 1874, p. 21.

† Divers, Proceedings of the Royal Society, xix. 425; Chem. Soc. Journ., 1871, p. 484.

The specific gravity of nitrogen dioxide is 1·039; a litre weighs 1·34343 grams. It contains equal measures of oxygen and nitrogen gases united without condensation. When this gas is passed into the solution of a ferrous salt, it is absorbed in large quantity, and a deep brown, or nearly black liquid produced, which seems to be a definite compound of the two substances (p. 160). The compound is decomposed by boiling.

Nitrogen Trioxide, or **Nitrous Oxide,** N_2O_3.—When four measures of nitrogen dioxide are mixed with one measure of oxygen, and the gases, perfectly dry, are exposed to a temperature of $-18°$, they condense to a thin mobile blue liquid, which emits orange-red vapours.

Nitrogen trioxide, sufficiently pure for most purposes, is obtained by pouring concentrated nitric acid on lumps of arsenious acid, and gently warming the mixture, in order to start the reaction. The trioxide is then evolved as an orange-red gas, arsenic acid remaining behind.

Nitrogen trioxide is decomposed by water, being converted into nitric acid and nitrogen dioxide: $3N_2O_3 + H_2O = 2HNO_3 + 2N_2O_2$. For this reason it cannot be made to unite directly with metallic oxides; potassium nitrite may, however, be prepared by fusing potassium nitrate, whereby part of its oxygen is driven off; and many other salts of nitrous acid may be obtained by indirect means. Thus a solution of potassium or sodium nitrite may be prepared by passing the vapour of nitrogen trioxide, obtained as above by heating nitric acid with arsenious acid (or with starch), into a solution of caustic potash or soda.

Nitrogen Tetroxide, N_2O_4 or NO_2 also called *Nitric Peroxide.*—This is the principal constituent of the deep red fumes always produced when nitrogen dioxide escapes into the air.

It may be obtained in the pure state :—1. By exposing a mixture of 2 vols. nitrogen dioxide and 1 vol. oxygen incorporated by passing through a tube filled with broken porcelain, and thoroughly dried by transmission over pumice soaked in oil of vitriol and then over recently fused stick potash, to the action of a freezing mixture of salt and ice; the tetroxide condenses in transparent crystals, or if the slightest trace of moisture is present, into an almost colourless liquid. 2. By the direct combination of oxygen with the trioxide, as when a stream of oxygen is passed into the mixture of the trioxide and other oxides of nitrogen evolved by the action of fuming nitric acid on arsenious acid. The liquid tetroxide thus obtained is pure enough for most purposes after one distillation. 3. By heating thoroughly dried lead nitrate in a retort, whereby a mixture of the tetroxide and oxygen is evolved, the former of which may be condensed as above, while the latter passes on:

$$(NO_3)_2Pb = PbO + O + N_2O_4.$$

The first portions of nitrogen tetroxide thus obtained do not solidify, doubtless owing to the presence of a trace of moisture, but if the receiver be changed in the midst of the operation, and if every care has been taken to avoid moisture, the later portions may be obtained in the crystalline form.

Nitrogen tetroxide at very low temperatures forms transparent, colourless, prismatic crystals which melt at −9°, but when once melted do not resolidify till cooled down to −30°. Above −9° it forms a mobile liquid of specific gravity 1·451, the appearance of which varies greatly according to the temperature. When still liquid below −9°, it is almost colourless; at −9° it has a perceptible greenish-yellow tint; at 0° the colour is somewhat more marked; at 10° it is decidedly yellow; and at 15° and upwards, orange-yellow, the depth of colour increasing progressively with the temperature up to 22°, the boiling point of the liquid. The vapour has a brown-red colour, the depth of which also increases with the temperature, until at 40° it is so dark as to be almost opaque. This remarkable change of colour is accompanied by a great diminution of density as the temperature rises, both phenomena pointing to a molecular change produced in the vapour by heat. Messrs Playfair and Wanklyn have determined the density of the vapour by Dumas' method, using nitrogen as a diluent (p. 54), and find that the densities at different temperatures are as follows:—

Temperature.	Vapour-density.
97·5°	1·783
24·5	2·520
11·3	2·645
4·2	2·588

Its vapour is absorbed by strong nitric acid, which thereby acquires a yellow or red tint, passing into green, then into blue, and afterwards disappearing altogether on the addition of successive portions of water. The deep red fuming acid of commerce, called *nitrous acid*, is simply nitric acid impregnated with nitrogen tetroxide.

Nitrogen tetroxide is decomposed by water at very low temperatures in such a manner as to yield nitric and nitrous acids, $N_2O_4 + H_2O = HNO_3 + HNO_2$; but when added to excess of water at ordinary temperatures it yields nitric acid, and the products of decomposition of nitrous acid, namely, nitric acid and nitrogen dioxide. In like manner, when passed into alkaline solutions, it forms a nitrate and a nitrite of the alkali-metal; but it has been also supposed to unite directly, under certain circumstances, with metallic oxides—lead oxide, for example—forming definite crystalline salts, and has hence been called *hyponitric acid;* but it is most probable that these salts are compounds of nitrates and nitrites: *e.g.*,

$$\underset{\text{Lead hyponitrate.}}{2(PbO.N_2O_4)} = \underset{\text{Lead nitrate.}}{Pb(NO_3)_2} + \underset{\text{Lead nitrite.}}{Pb(NO_2)_2}$$

Nitrogen appears to combine, under favourable circumstances, with metals. When iron is heated to redness in an atmosphere of ammonia, it becomes brittle and crystalline, and shows an increase in weight, said to vary from 6 to 12 per cent.; while, according to other observers, the physical characters of the metal are changed without sensible alteration of weight. By heating copper in ammonia, no compound of nitrogen with copper is produced; but when ammonia is passed over copper oxide heated to 300°, water is formed, and a soft brown powder produced, which, when heated further, evolves nitrogen, and leaves metallic copper. The same effect is produced by the contact of strong acids. A similar compound of chromium with nitrogen appears to exist.

NITROGEN AND HYDROGEN; AMMONIA, NH_3.

When powdered sal-ammoniac is mixed with moist calcium hydrate (slaked lime), and gently heated in a glass flask, a large quantity of gaseous matter is disengaged, which must be collected over mercury, or by displacement, advantage being taken of its low specific gravity.

Ammonia gas thus obtained is colourless; it has a strong pungent odour, and possesses in an eminent degree those properties to which the term *alkaline* is applied; that is to say, it turns the yellow colour of turmeric to brown, that of reddened litmus to blue, and combines readily with acids, neutralising them completely; by these reactions it is easily distinguished from all other bodies possessing the same physical characters. Under a pressure of 6·5 atmospheres at 15·5°, ammonia condenses to the liquid form. Water dissolves about 700 times its volume of this gas, forming a solution which in a more dilute state has long been known under the name of *liquor ammoniæ*; by heat a great part is again expelled. The solution is decomposed by chlorine, sal-ammoniac being formed, and nitrogen set free.

Ammonia has a density of 0·589; a litre weighs 0·76271 gram. It cannot be formed by the direct union of its elements, although it is sometimes produced under rather remarkable circumstances by the deoxidation of nitric acid.* The great sources of ammonia are the feebly compounded azotised principles of the animal and vegetable kingdoms, which, when left to putrefactive change, or subjected to destructive distillation, almost invariably give rise to an abundant production of this substance.

The analysis of ammonia gas is easily effected. When a portion is confined in a graduated tube over mercury, and electric sparks are passed through it for a considerable time, the volume of the gas gradually increases until it becomes doubled. On examination the tube is found to contain a mixture of 3 measures of hydrogen gas and 1 measure of nitrogen. Every two volumes of the ammonia, therefore, contained three volumes of hydrogen and one of nitrogen, the whole being condensed to one half. The weight of the two constituents is in the proportion of 3 parts hydrogen to 14 parts nitrogen.

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* A mode of converting the nitrogen of the atmosphere into ammonia, by a succession of chemical operations, will be noticed in connection with Cyanogen under Organic Chemistry.

Ammonia may also be decomposed into its elements by transmission through a red-hot tube.

Solution of ammonia is a very valuable reagent, and is employed in a great number of chemical operations, for some of which it is necessary to have it perfectly pure. The best mode of preparation is the following:—

Equal weights of sal-ammoniac (NH_4Cl), and quicklime (CaO), are taken; the lime is slaked in a covered basin, and the salt reduced to powder. These are mixed and introduced into a large flask connected with a wash-bottle and a receiver containing water, in the manner which will be described in connection with hydrochloric acid (fig. 117, p. 190.) A little water is added to the mixture, just enough to damp it and cause it to aggregate into lumps. On cautiously applying heat to the flask, ammonia is disengaged very regularly and uniformly, and condenses in the water of the receiver. Calcium chloride ($CaCl_2$), with excess of calcium hydrate (slaked lime) remains in the flask.

The decomposition of the salt is represented by the equation:—

$$2NH_4Cl + CaO = 2NH_3 + CaCl_2 + H_2O.$$

Solution of ammonia should be perfectly colourless, leave no residue on evaporation, and when supersaturated by nitric acid, give no cloud or muddiness with silver nitrate. Its density diminishes with its strength, that of the most concentrated being about 0·875. The value in alkali of any sample of liquor ammoniæ is most safely inferred, not from a knowledge of its density, but from the quantity of acid a given amount will saturate. The mode of conducting this experiment will be described under *Alkalimetry*.

When solution of ammonia is mixed with acids of various kinds, salts are generated, which resemble in the most complete manner the corresponding potassium and sodium compounds: they are best discussed in connection with the latter. The ammonia salts may be regarded either as direct compounds of ammonia, NH_3, with acids (HCl, for example), or as resulting from the replacement of the hydrogen of an acid by the group NH_4, called *ammonium*, which in this sense is a compound metal, chemically equivalent to potassium, sodium, silver, &c. Thus:—

Ammonia hydrochloride $NH_3.HCl$ = $NH_4.Cl$ **Ammonium chloride.**
,, **nitrate** $NH_3.HNO_3$ = $NH_4.NO_3$,, **nitrate.**
,, **sulphate** $(NH)_2 H_2SO_4$ = $(NH_4)_2.SO_4$,, **sulphate.**

The formulæ in the second column are exactly analogous to those of the potassium salts, KCl, KNO_3, K_2SO_4.

The aqueous solution of ammonia may be supposed to contain the *hydrate of ammonium* $NH_4.HO$; but this compound is not known in the solid state.

Any ammoniacal salt can at once be recognised by the evolution of ammonia which takes place when it is heated with slaked lime, or solution of potash or soda.

HYDROXYLAMINE, NH_3O.

THIS compound, intermediate in composition between ammonia NH_3, and ammonium hydrate $NH_4.HO$, is formed by the direct union of hydrogen with nitrogen dioxide : $NO + H_3 = NH_3O$, and may be prepared by passing nitrogen dioxide through a series of flasks in which hydrogen is evolved by heating hydrochloric acid with tin. The resulting liquid is freed from tin by hydrogen sulphide ; the filtered liquid evaporated to dryness ; the residue washed with cold alcohol, and digested with boiling alcohol; the alcoholic solution mixed with platinic chloride to precipitate sal-ammoniac; and the filtered alcoholic liquid mixed with ether, which throws down pure hydrochloride of hydroxylamine.

Hydroxylamine is also formed by the action of hydrogen (evolved as above) on nitric acid or ethyl nitrate:

$$NO_3H + 6H = 2H_2O + NH_3O.$$

Hydroxylamine is a very volatile and easily decomposible base, and can be obtained only in solution. Its salts are decomposed by potash, with evolution of nitrogen and formation of ammonia, quickly in concentrated, gradually in dilute solutions. Solutions of hydroxylamine may, however, be obtained by decomposing the salts in other ways, an alcoholic solution, for example, by decomposing the nitrate dissolved in alcohol with alcoholic potash. Alkaline carbonates also separate hydroxylamine, with evolution of carbon dioxide. The solutions have an alkaline reaction, and precipitate many metallic salts; with the salts of lead, iron, nickel, and zinc, and with chrome-alum and common alum, they form precipitates insoluble in excess of hydroxylamine. With aqueous cupric sulphate, hydroxylamine forms a grass-green precipitate, which when boiled with water, is reduced, with evolution of gas, to cuprous oxide; an ammoniacal cupric solution is decolorised by it. Mercuric chloride is reduced to mercurous chloride, and if the hydroxylamine is in excess, to metallic mercury. Silver solutions yield a black precipitate, which is quickly reduced, with evolution of gas, to metallic silver. Hydroxylamine also reduces acid potassium chromate. In many of these reactions the hydroxylamine appears to be completely decomposed, with formation of nitrogen or its monoxide.

The salts of hydroxylamine decompose when heated, with copious and sudden evolution of gas; most of them easily form supersaturated solutions; none of those yet examined contain water of crystallisation. The *hydrochloride*, $NH_3O.HCl$, crystallises from alcohol in long spicular crystals resembling urea; from water in large irregular six-sided tables; it melts at 100°, and then decomposes, with violent evolution of gas, into nitrogen, hydrochloric acid, water, and sal-ammoniac. The *nitrate*, $NH_3O.HNO_3$, solidifies slowly by spontaneous evaporation to a radio-crystalline, very deliquescent mass, easily soluble in absolute alcohol, decomposing at 100.

CARBON.

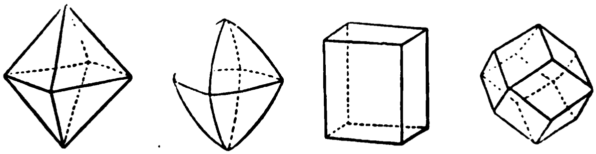
Atomic weight, 12. Symbol C.

THIS substance occurs in a state of purity, and crystallised, in two distinct and very dissimilar forms—namely, as diamond, and as graphite or plumbago. It constitutes a large proportion of all organic structures, animal and vegetable: when these latter are exposed to destructive distillation in close vessels, a great part of their carbon remains, obstinately retaining some of the hydrogen and oxygen, and associated with the earthy and alkaline matter of the tissue, giving rise to the many varieties of charcoal, coke, &c. This residue, when perfectly separated from foreign matter, constitutes a third variety of carbon.

The diamond is one of the most remarkable substances known: long prized on account of its brilliancy as an ornamental gem, the discovery of its curious chemical nature confers upon it a high degree of scientific interest. Several localities in India, the Island of Borneo, South Africa, and Brazil, furnish this beautiful substance. It is always distinctly crystallised, often quite transparent and colourless, but now and then having a shade of yellow, pink, or blue. The origin or true geological position of the diamond are unknown; it is always found imbedded in gravel and transported materials whose history cannot be traced. The crystalline form of the diamond is that of the regular octohedron or cube, or some figure geometrically connected with these. Many of the octohedral crystals exhibit a very peculiar appearance, arising from the faces being curved or rounded, which gives to the crystal an almost spherical figure.

The diamond is infusible and unalterable even by a very intense heat, provided air be excluded; but when heated, thus protected, between the poles of a strong galvanic battery, it is converted into coke or graphite; heated to whiteness in a vessel of oxygen, it burns with facility, yielding carbonic acid gas.

Fig. 103.



The diamond is the hardest substance known: it admits of being split or cloven without difficulty in particular directions, but can only be cut or abraded by a second portion of the same material; the powder rubbed off in this process serves for polishing the new faces, and is also highly useful to the lapidary and seal-engraver. One very curious and useful application of the diamond is made by the glazier: a *fragment* of this mineral, like a bit of flint, or any other hard substance, scratches the surface of the glass; a *crystal* of diamond, having the rounded octohedral figure spoken of, held in one particular position on the glass—namely, with an edge formed by the meeting of two adjacent faces presented to the surface—and, then drawn along with gentle pressure, causes a split or cut, which penetrates to a considerable depth into the glass, and determines its fracture with perfect certainty.

Graphite or plumbago appears to consist essentially of pure carbon, although most specimens contain iron, the quantity of which varies from a mere trace up to five per cent. Graphite is a somewhat rare mineral; the finest and most valuable for pencils was formally obtained from Borrowdale, in Cumberland, where a kind of irregular vein is found traversing the ancient slate beds of that district, but the mine is now nearly exhausted. Large quantities of graphite are imported from Germany, the East Indies, and the United States.* Crystals are not common: when they occur, they have the figure of a short six-sided prism—a form bearing no geometric relation to that of the diamond.

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* The graphite which can be directly cut for pencils occurring only in limited quantity, powdered graphite, obtained from the inferior varieties of the mineral, is now frequently consolidated for this purpose. The mechanical division of graphite presents considerable difficulties, which may be entirely obviated by adopting a chemical process suggested by Sir Benjamin Brodie, applicable, however, only to certain varieties, such as Ceylon and Siberian graphite. This process consists in introducing the coarsely powdered graphite. previously mixed with $\frac{1}{14}$ of its weight of potassium chlorate, into 2 parts of concentrated sulphuric acid, which is heated in a water-bath until the evolution of acid fumes ceases. The acid is then removed by water, and the graphite dried. Thus prepared, this substance, when heated to a temperature approaching a red-heat, swells up to a bulky mass of finely divided graphite.

Graphite is often formed artificially in certain metallurgic operations: the brilliant scales which sometimes separate from melted cast-iron on cooling, called by the workmen "kish," consist of graphite.

Lamp-black, the soot produced by the imperfect combustion of oil or resin, is the best example that can be given of carbon in its uncrystallised or *amorphous* state. To the same class belong the different kinds of charcoal. That prepared from wood, either by distillation in a large iron retort, or by the smothered combustion of a pile of faggots partially covered with earth, is the most valuable as fuel. Coke, the charcoal of pit-coal, is much more impure; it contains a large quantity of earthy matter, and very often sulphur, the quality depending very much upon the mode of preparation. Charcoal from bones and animal matters in general is a very valuable substance, on account of the extraordinary power it possesses of removing colouring matters from organic solutions; it is used for this purpose by the sugar-refiner to a very great extent, and also by the manufacturing and scientific chemist. The property in question is possessed by all kinds of charcoal in a small degree.

Charcoal made from box, or other dense wood, has the property of condensing gases and vapours into its pores; of ammoniacal gas it is said to absorb not less than ninety times its volume, while of hydrogen it takes up less than twice its own bulk, the quantity being apparently connected with the property in the gas of suffering liquefaction. This property of absorbing gases, as well as the decolorising power, no doubt depends in some way upon the same peculiar action of surface so remarkable in the case of platinum in a mixture of oxygen and hydrogen. The absorbing power is, indeed, considerably increased by saturating charcoal with solution of platinum, and subsequently igniting it, so as to coat the charcoal with a thin film of platinum. Dr. Stenhouse, who suggested this plan, finds that the gases thus absorbed undergo a kind of oxidation within the pores of the charcoal.

Compounds of Carbon and Oxygen.

There are two direct inorganic compounds of carbon and oxygen, called carbon monoxide and carbon dioxide; their composition may be thus stated:

	By weight.	
	Carbon.	Oxygen.
Carbon monoxide, CO . .	12	16
Carbon dioxide, CO_2 . .	12	32

Carbon Dioxide or **Carbonic Anhydride**—(commonly called *Carbonic Acid*), is always produced when charcoal burns in air or oxygen gas: it is most conveniently obtained, however, by decomposing a carbonate with one of the stronger acids. For this purpose the apparatus for generating hydrogen (p. 129), may again be employed: fragments of marble are put into the bottle with enough water to cover the extremity of the funnel-tube, and hydrochloric or nitric acid is added by the latter, until the gas is freely disengaged. Chalk-powder and dilute sulphuric acid may be used instead. The gas may be collected over water, although with some loss; or very conveniently by displacement, if it be required dry, as shown in fig. 105. The long drying-tube is filled with fragments of calcium chloride, and the heavy gas is conducted to the bottom of the vessel in which it is to be received, the mouth of the latter being lightly closed.*

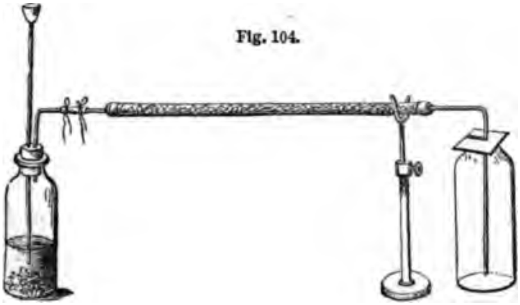

Fig. 104.

Carbon dioxide is a colourless gas; it has an agreeable pungent taste and odour, but cannot be respired for a minute without insensibility following. Its specific gravity is 1·524; a liter weighs 1·96664 grams, and 100 cubic inches weigh 47·26 grains.

This gas is very hurtful to animal life, even when largely diluted with air; it acts as a narcotic poison: hence the danger arising from imperfect ventilation, the use of fire-places and stoves of all kinds unprovided with proper chimneys, and the crowding together of many individuals in houses and ships without efficient means for renewing the air: for carbon dioxide is constantly disengaged during the process of respiration, which, as already mentioned (p. 121), is nothing but a process of slow combustion. This gas is sometimes emitted in large quantity from the earth in volcanic districts, and it is constantly generated where organic matter is in the act of undergoing fermentive decomposition. The fatal "after-damp" of the coal-mines contains a large proportion of carbon dioxide.

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* In connecting tube-apparatus for conveying gases or cold liquids, not corrosive, tubes of vulcanised caoutchouc, which are now articles of commerce, are very serviceable. Glass tubes are easily bent in the flame of a spirit-lamp, or a Bunsen burner, and, when necessary, cut by scratching with a file and broken asunder.

A lighted taper plunged into carbon dioxide is instantly extinguished even to the red-hot snuff. The gas, when diluted with three times its volume of air, still retains the power of extinguishing a light. It is easily distinguished from nitrogen, which is also incapable of supporting combustion, by its rapid absorption by caustic alkali, or by lime-water; the turbidity communicated to the latter from the production of insoluble calcium carbonate is very characteristic.

Cold water dissolves about its own volume of carbon dioxide, whatever be the density of the gas with which it is in contact (comp. p. 148); the solution temporarily reddens litmus paper. In common soda-water, and in effervescent wines, examples may be seen of the solubility of the gas. Even boiling water absorbs a perceptible quantity.

Some of the interesting phenomena attending the liquefaction of carbon dioxide have been already described (p. 49): it requires for the purpose a pressure of 38·5 atmospheres at 0°. The liquefied oxide is colourless and limpid, lighter than water, and four times more expansible than air; it mixes in all proportions with ether, alcohol, naphtha, oil of turpentine, and carbon disulphide, and is insoluble in water and fat oils. In this condition it does not exhibit any of the properties of an acid.

Carbon dioxide exists, as already mentioned, in the air: relatively its quantity is but small; but absolutely, taking into account the vast extent of the atmosphere, it is very great, and fully adequate to the purpose of supplying plants with their carbon, these latter having the power, by the aid of their green leaves, of decomposing carbon dioxide, retaining the carbon, and expelling the oxygen. The presence of light is essential to this effect, but of the manner in which it is produced we are yet ignorant.

The carbonates form a very large and important group of salts, some of which, as the carbonates of calcium and magnesium, occur very abundantly in nature. They contain the elements of carbon dioxide and a metallic oxide: calcium carbonate, for example, being composed of 56 parts of calcium oxide or lime, and 44 parts by weight of carbon dioxide, or of 40 calcium, 12 carbon, and 48 oxygen, a composition which is represented by the formula $CaO.CO_2$ or $CaCO_3$; but they are never formed by the direct union of dry carbon dioxide with a dry metallic oxide, the intervention of water being always required to bring about the combination. Potassium carbonate (pearlash) is the chief constituent of wood-ashes; sodium carbonate is contained in the ashes of marine plants, and is manufactured on a very large scale by heating sodium sulphate with lime and coal. These carbonates are soluble in water. The other metallic carbonates, which are insoluble, may be formed by mixing a solution of potassium or sodium carbonate with a soluble metallic salt; thus, when solutions of lead nitrate and sodium carbonate are mixed together, the lead and sodium change places, forming sodium nitrate, which remains dissolved, and lead carbonate, which, being insoluble in water, is precipitated in the form of a white powder: $Pb(NO_3)_2 + Na_2CO_3 = 2NaNO_3 + PbCO_3$.

This is an example of *double decomposition*, the most frequent of all forms of chemical action.

The solution of carbon dioxide in water may be supposed to contain hydrogen carbonate or carbonic acid, consisting of 2 parts by weight of hydrogen, 12 carbon, and 48 oxygen, and represented by the formula H_2CO_3 or $H_2O.CO_2$; but this compound is not known in the separate state, only in aqueous solution.

Carbon Monoxide (commonly called *Carbonic Oxide.*)—When carbon dioxide is passed over red-hot charcoal or metallic iron, one half of its oxygen is removed, and it becomes converted into carbon monoxide. A very good method of preparing this gas is to introduce into a flask fitted with a bent tube some crystallised oxalic acid ($H_2C_2O_4$), and pour upon it five or six times as much strong oil of vitriol. On heating the mixture, the oxalic acid is resolved into water, carbon dioxide, and carbon monoxide. $H_2C_2O_4 = CO + CO_2 + H_2O$: and by passing the gases through a strong solution of caustic potash, the first is withdrawn by absorption, while the second remains unchanged. Another and, it may be, preferable method, is to heat finely powdered yellow potassium ferrocyanide with eight or ten times its weight of concentrated sulphuric acid. The salt is entirely decomposed, yielding a most copious supply of perfectly pure carbon monoxide, which may be collected over water in the usual manner. The reaction is represented by the equation—

$$\underset{\substack{\text{Potassium ferro-}\\\text{cyanide.}}}{K_4FeC_6N_6} + 6H_2O + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{6H_2SO_4} = 6CO + \underset{\substack{\text{Potassium}\\\text{sulphate.}}}{2K_2SO_4} + \underset{\substack{\text{Ammonium}\\\text{sulphate.}}}{3(NH_4)_2SO_4} + \underset{\substack{\text{Ferrous}\\\text{sulphate.}}}{FeSO_4}$$

Carbon monoxide is a combustible gas, which burns with a beautiful pale-blue flame, generating carbon dioxide. It has never been liquefied. It is colourless, has very little odour, and is extremely poisonous—much more so than carbon dioxide. Mixed with oxygen, it explodes by the electric spark, but with some difficulty. Its specific gravity is 0·973; a liter weighs 1·2515 grams; 100 cubic inches weigh 30·21 grains.

The relation by volume of these oxides of carbon is as follows:—Carbon dioxide contains its own volume of oxygen, that gas suffering no change of bulk by its conversion. One measure of carbon monoxide, mixed with half a measure of oxygen and exploded, yields one measure of carbon dioxide: hence carbon monoxide contains half its volume of oxygen.

Carbon monoxide unites with chlorine under the influence of light, forming a pungent, suffocating compound, possessing acid properties, called phosgene gas, or carbonyl chloride, $COCl_2$. It is made by mixing equal volumes of carbon monoxide and chlorine, both perfectly dry, and exposing the mixture to sunshine: the gases unite quietly, the colour disappears, and the volume becomes reduced to one-half. A more convenient method of preparing this gas consists in passing carbon monoxide through antimony pentachloride. It must be received over mercury, as it is decomposed by water. When pure it condenses to a liquid at 0°; or more quickly at the temperature of a mixture of ice and salt.

Compounds of Carbon and Hydrogen.

The compounds of carbon and hydrogen already known are exceedingly numerous: perhaps all, in strictness, belong to the domain of organic chemistry, as they cannot, except in very few cases, be formed by the direct union of their elements, but always arise from the decomposition of a complex body of organic origin. It will be found convenient, notwithstanding, to describe three of them in this part of the volume, as they very well illustrate the important subjects of combustion and the nature of flame.

Methane or **Marsh Gas**; *Light Carburetted Hydrogen; Fire-damp*, CH_4.—This gas is but too often found to be abundantly disengaged in coal mines from the fresh-cut surface of the coal, and from remarkable apertures or "blowers," which emit for a great length of time a copious stream or jet of gas, probably existing in a state of compression, pent up in the coal.

When the mud at the bottom of pools in which water-plants grow is stirred, bubbles of gas escape, which may be easily collected. This, on examination, is found to be chiefly a mixture of light carburetted hydrogen and carbon dioxide: the latter is easily absorbed by lime water or caustic potash.

For a long time, no method was known by which methane could be produced in a state approaching to purity by artificial means; the various illuminating gases from pit-coal and oil, and that obtained by passing the vapour of alcohol through a red-hot tube, contain large quantities of it, associated, however, with other substances which hardly admit of separation; but Dumas has discovered a method by which it can be produced perfectly pure, and in any quantity.

A mixture is made of 40 parts crystallised sodium acetate, 40 parts solid sodium hydroxide and 60 parts quicklime in powder. This mixture is transferred to a flask or retort, and strongly heated; the gas is disengaged in great abundance, and may be collected over water, while sodium carbonate remains behind. The reaction is represented by the equation—

$$\underset{\substack{\text{Sodium}\\\text{acetate.}}}{NaC_2H_3O_2} + \underset{\substack{\text{Sodium}\\\text{hydroxide.}}}{NaHO} = \underset{\substack{\text{Marsh}\\\text{gas.}}}{CH_4} + \underset{\substack{\text{Sodium}\\\text{carbonate.}}}{Na_2CO_3}$$

The use of the lime is merely to prevent the soda from fusing and attacking the glass.

Methane is a colourless and nearly inodorous gas, which does not affect vegetable colours. It burns with a yellow flame, generating carbon dioxide and water. It is not poisonous, and may be respired to a great extent without apparent injury. The density of this compound is about 0·559, a liter weighing 0·71558 grams, and 100 cubic inches weighing 17·41 grains; it contains carbon and hydrogen associated in the proportion of 12 parts by weight of the former to 4 of the latter.

When 100 measures of this gas are mixed with 200 of pure oxygen in the eudiometer, and the mixture exploded by the electric spark, 100 measures of gas remain, which are entirely absorbable by a little solution of caustic potash. Now, carbon dioxide contains its own volume of oxygen: hence one-half the oxygen added—that is, 100 measures—must have been consumed in uniting with the hydrogen. Consequently, the gas must contain twice its own measure of hydrogen, and enough carbon to produce, when completely burned, an equal quantity of carbon dioxide.

When chlorine is mixed with marsh gas over water, no change follows, provided light be excluded. The presence of light, however, brings about decomposition, hydrochloric acid, carbon dioxide, and other products, being formed. It is important to remember that this gas is not acted upon by chlorine in the dark.

Ethene, or Olefiant Gas, C_2H_4.—Strong spirit of wine is mixed with five or six times its weight of oil of vitriol in a glass flask, the tube of which passes into a wash-bottle containing caustic potash. A second wash-bottle, partly filled with oil of vitriol, is connected with the first, and furnished with a tube dipping into the water of the pneumatic trough. On the first application of heat to the contents of the flask, alcohol, and afterwards ether, make their appearance; but, as the temperature rises, and the mixture blackens, the ether-vapour diminishes in quantity, and its place becomes in great part supplied by a permanent inflammable gas; carbon dioxide and sulphurous oxide are also generated at the same time, besides traces of other products. The two last-mentioned gases are absorbed by the alkali in the first bottle, and the ether-vapour by the acid in the second, so that the olefiant gas is delivered tolerably pure. The entire reaction is too complex to be discussed at the present moment; it will be found fully described in the second volume; but the ethene may be regarded as resulting from a simple dehydration of the alcohol by the oil of vitriol.

$$\underset{\text{Alcohol.}}{C_2H_6O} = \underset{\text{Ethene.}}{C_2H_4} + \underset{\text{Water.}}{H_2O}$$

Olefiant gas thus produced is colourless, neutral, and but slightly soluble in water. Alcohol, ether, oil of turpentine, and even olive oil, dissolve it to a considerable extent. It has a faint odour of garlic. On the approach of a kindled taper it takes fire, and burns with a splendid white light, far surpassing in brilliancy that produced by marsh gas. This gas, when mixed with oxygen and fired, explodes with extreme violence. Its density is 0·981; a liter weighs 1·25194 grams; 100 cubic inches weigh 30·57 grains.

By the use of the eudiometer, as already described, it has been found that each measure of ethene requires for complete combustion exactly three of oxygen, and produces under these circumstances two measures of carbon dioxide: whence it is evident that it contains twice its own volume of hydrogen combined with twice as much carbon as in methane.

By weight, these proportions are 24 parts carbon and 4 parts hydrogen.

Ethene is decomposed by passing it through a tube heated to bright redness; a deposit of charcoal and tar takes place, and the gas becomes converted into marsh gas, or even into free hydrogen, if the temperature be very high. This latter change is, of course, attended by increase of volume.

Chlorine acts upon ethene in a very remarkable matter. When the two bodies are mixed, even in the dark, they combine in equal measures, and give rise to a heavy oily liquid, of sweetish taste and ethereal odour, to which the name of ethene chloride, or Dutch liquid, $C_2H_4Cl_2$, is given. It is from this peculiarity that the term *olefiant* gas is derived.

On mixing in a tall jar two measures of chlorine and one of ethene, and then quickly applying a light to the mouth of the vessel, the chlorine and hydrogen unite with flame, which passes quickly down the jar, while the whole of the carbon is set free in the form of a thick black smoke.

Ethine or **Acetylene**, C_2H_2.—This hydro-carbon is formed by the direct union of its elements. Hydrogen and carbon do not combine at ordinary temperatures, or even under the influence of the most intense heat; but when an electric arc from a very powerful voltaic battery is passed between carbon poles in a current of hydrogen, the carbon and hydrogen unite to form acetylene. This compound is carried forward by the stream of hydrogen, and on passing the mixed gases into a solution of cuprous chloride, the acetylene is separated in the form of a red solid copper compound, which, when decomposed by hydrochloric acid, yields pure acetylene.

Acetylene is a colourless gas of specific gravity 0·92. It burns in the air with a bright smoky flame, and when mixed with chlorine, detonates almost instantly, even in diffused daylight, with separation of carbon.

Acetylene is one of the constituents of coal-gas, and is produced in the imperfect combustion of various bodies containing carbon and hydrogen. The modes of formation, reactions, and derivatives of this compound will be further considered under Organic Chemistry.

Coal and Oil Gases.—The manufacture of coal gas is a branch of industry of great interest and importance in several points of view. The process is one of great simplicity of principle, but requires, in practice, some delicacy in management to yield a good result.

When pit-coal is subjected to destructive distillation, a variety of products show themselves—permanent gases, steam and volatile oils, besides a not inconsiderable quantity of ammonia from the nitrogen always present in the coal. These substances vary very much in their proportions with the temperature at which the process is conducted, the permanent gases becoming more abundant with increased heat, but, at the same time, losing much of their value for the purposes of illumination.

The coal is distilled in cast-iron retorts, maintained at a bright-red heat, and the volatilised product is conducted into a long horizontal pipe of large dimensions, always half filled with liquid, into which the extremity of each separate tube dips: this is called the hydraulic main. The gas and its accompanying vapours are next made to traverse a refrigerator—usually a series of iron pipes, cooled on the outside by a stream of water; here the condensation of the tar and the ammoniacal liquid becomes complete, and the gas proceeds onwards to another part of the apparatus, in which it is deprived of the sulphuretted hydrogen and carbonic acid always present in the crude product. This separation was formerly effected by slaked lime, which readily absorbs the compounds in question. The use of lime, however, has been almost superseded by that of a mixture of sawdust and iron oxide. This mixture, after having been used, is exposed for some time to the atmosphere, and is then fit for use a second time. The purifiers are large iron vessels filled either with slaked lime or with the iron oxide mixture. The gas is admitted at the bottom of the vessel, and made to pass over a large surface of the purifying agents. The last part of the operation, which, indeed, is often omitted, consists in passing the gas through dilute sulphuric acid, in order to remove ammonia. The quantity thus separated is very small, relatively, to the bulk of the gas, but, in an extensive work, becomes an object of importance.

Coal-gas thus manufactured and purified is preserved for use in immense cylindrical receivers, closed at the top, suspended in tanks of water by chains to which counterpoises are attached, so that the gas-holders rise and sink in the liquid as they become filled from the purifiers or emptied by the mains. These latter are made of large diameter, to diminish as much as possible the resistance experienced by the gas in passing through such a length of pipe. The joints of these mains are still made in so imperfect a manner that immense loss is experienced by leakage when the pressure upon the gas exceeds that exerted by a column of water an inch in height.*

Coal gas varies very much in composition, judging from its variable density and illuminating powers, and from the analyses which have been made. The difficulties of such investigations are very great, and unless particular precaution be taken, the results are merely approximate. The purified gas is believed to contain the following substances, of which the first is the most abundant and the second the most valuable:—

Methane, or Marsh gas.
Ethene, or Olefiant gas.
Ethine, or Acetylene.
Hydrogen.
Carbon Monoxide.
Nitrogen.
Vapours of volatile liquid Hydrocarbons.†
Vapour of Carbon Bisulphide.

Separated by Condensation and by the Purifiers.

Tar and Volatile Oils.
Ammonium Sulphate, Chloride, and Sulphide.
Hydrogen Sulphide.
Carbon Dioxide.
Hydrocyanic acid, or Ammonium Cyanide.
Sulphocyanic acid, or Ammonium Sulphocyanate.

A far better illuminating gas may be prepared from oil, by dropping it into a red-hot iron retort filled with coke; the liquid is in great part decomposed and converted into permanent gas, which requires no purification, as it is quite free from the ammoniacal and sulphur compounds which vitiate gas from coal. Many years ago this gas was prepared in London; it was compressed, for the use of the consumer, into strong iron vessels, to the extent of 30 atmospheres; these were furnished with a screw-valve of peculiar construction, and exchanged for others when exhausted. The comparative high price of the material, and other circumstances, led to the abandonment of the undertaking. On the Continent gas is now extensively prepared from wood.

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* It may give some idea of the extent of this species of manufacture, to mention that in the year 1838, for lighting London and the suburbs alone, there were eighteen public gas-works, and £2,800,000 invested in pipes and apparatus. The yearly revenue amounted to £450,000, and the consumption of coal in the same period to 180,000 tons, 1460 *millions* of cubic feet of gas being made in the year. There were 134,300 private lights, and 30,400 street lamps. 890 tons of coals were used in the retorts in the space of twenty-four hours at mid-winter, and 7,120,000 cubic feet of gas consumed in the longest night.—*Ure, Dictionary of Arts and Manufactures.*

Since that time, the production of gas has been enormously increased. The amount of coal used in London for gas-making in the year ending June 1852 is estimated at 408,000 tons, which on an average would yield about 4000 *millions* of cubic feet of gas. In the year 1857 the mains in the London streets had reached the extraordinary length of 2000 miles.

† These bodies increase the illuminating power, and confer on the gas its peculiar odour.

Combustion, and the Structure of Flame.

When any solid substance capable of bearing the fire is heated to a certain point, it emits light, the character of which depends upon the temperature. Thus, a bar of platinum or a piece of porcelain, raised to a particular temperature, becomes what is called red-hot, or emissive of red light: at a higher degree of heat, this light becomes whiter and more intense, and when urged to the utmost, as in the case of a piece of lime placed in the flame of the oxyhydrogen blow-pipe, the light becomes exceedingly powerful, and acquires a tint of violet. Bodies in these states are said to be *incandescent* or *ignited.*

Again, if the same experiment be made on a piece of charcoal, similar effects will be observed; but something in addition; for whereas the platinum and porcelain, when removed from the fire, or the lime from the blow-pipe flame, begin immediately to cool, and emit less and less light, until they become completely obscure, the charcoal maintains to a great extent its high temperature. Unlike the other bodies, too, which suffer no change whatever, either of weight or substance, the charcoal gradually wastes away until it disappears. This is what is called *combustion,* in contradistinction to mere ignition; the charcoal burns, and its temperature is kept up by the heat evolved in the act of union with the oxygen of the air.

In the most general sense, a body in a state of combustion is one in the act of undergoing intense chemical action: any chemical action whatsoever, if its energy rise sufficiently high, may produce the phenomenon of combustion, by *heating the body to such an extent that it becomes luminous.*

In all ordinary cases of combustion, the action lies between the burning body and the oxygen of the air; and since the materials employed for the economical production of heat and light consist of carbon chiefly, or that substance conjoined with a certain proportion of hydrogen and oxygen, all common effects of this nature are cases of the rapid and violent oxidation of carbon and hydrogen by the aid of the free oxygen of the air. The heat must be referred to the act of chemical union, and the light to the elevated temperature.

By this principle, it is easy to understand the means which must be adopted to increase the heat of ordinary fires to the point necessary to melt refractory metals, and to bring about certain desired effects of chemical decomposition. If the rate of consumption of the fuel can be increased by a more rapid introduction of air into the burning mass, the intensity of the heat will of necessity rise in the same ratio, the quantity of heat evolved being fixed and definite for the same constant quantity of chemical action. This increased supply of air may be effected by two distinct methods: it may be forced into the fire by bellows or blowing-machines, as in the common forge and in the blast and cupola-furnaces of the iron-worker; or it may be drawn through the burning materials by the help of a tall chimney, the fireplace being closed on all sides, and no entrance of air allowed, save between the bars of the grate. Such is the kind of furnace generally employed by the scientific chemist in assaying and in the reduction of metallic oxides by charcoal: the principle will be at once understood by the aid of the sectional drawing (fig. 105), in which a crucible is represented arranged in the fire for an operation of the kind mentioned.

The "reverberatory" furnace (fig. 106) is one very much used in the arts when substances are to be exposed to heat without contact with the fuel. The fire-chamber is separated from the bed or hearth of the furnace by a low wall or *bridge* of brickwork, and the flame and heated air are reflected downwards by the arched form of the roof. Any degree of heat can be obtained in a furnace of this kind—from the temperature of dull redness to that required to melt very large quantities of cast-iron. The fire is urged by a chimney provided with a sliding-plate, or damper, to regulate the draught.

Fig. 105.

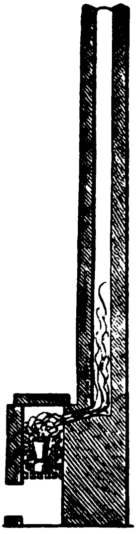
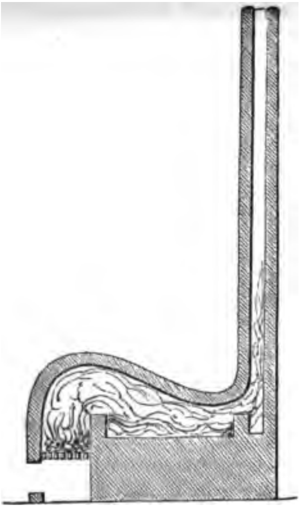


Fig. 106.



Solids and liquids, as melted metal, possess, when sufficiently heated, the faculty of emitting light: the same power is exhibited by gaseous bodies, but the temperature required to render a gas luminous is incomparably higher than in the cases already described. Gas or vapour in this condition constitutes *flame*, the actual temperature of which generally exceeds that of the white heat of solid bodies.

The light emitted from pure flame is often exceedingly feeble; but the illuminating power may be immensely increased by the presence of solid matter. The flame of hydrogen, or of the mixed gases, is scarcely visible in full daylight; in a dusty atmosphere, however, it becomes much more luminous by igniting to intense whiteness the floating particles with which it comes in contact. The piece of lime in the blow-pipe flame cannot have a higher temperature than that of the flame itself, yet the light it throws off is infinitely greater.

On the other hand, it is possible, as recently pointed out by Dr. Frankland, to produce very bright flames in which no solid particles are present. Metallic arsenic burnt in a stream of oxygen produces an intense white flame, although both the metal itself and the product of its combustion (arsenious oxide) are gaseous at the temperature of the flame. The combustion of a mixture of nitrogen dioxide and carbon bisulphide also produces a dazzling white flame, without any separation of solid matter.

The conditions most essential to luminosity in a flame are a high temperature, and the presence of gases or vapours of considerable density. The effect of high temperature is seen in the greater brightness of the flame of sulphur, phosphorus, and indeed all substances, when burnt in pure oxygen, as compared with that which results from their combustion in common air; in the former case the whole of the substances present take part in the combustion, and generate heat, whereas in the latter the temperature is lowered by the presence of a large quantity of nitrogen, which contributes nothing to the effect. The relation between the luminosity of a flame and the vapour-densities of its constituents may be seen from the following table, in which the vapour-densities are referred to that of hydrogen as unity.

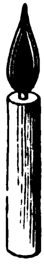
Relative Densities of Gases and Vapours.

Hydrogen,	1	Arsenious chloride,	90¾
Water,	9	Phosphoric oxide,	71, or 142
Hydrochloric acid,	18¼	Metallic arsenic,	150
Carbon dioxide,	22	Arsenious oxide,	198
Sulphur dioxide,	32		

A comparison of these numbers shows that the brightest flames are those which contain the densest vapours. Hydrogen burning in chlorine produces a vapour more than twice as heavy as that resulting from its combustion in oxygen, and accordingly the light produced in the former case is stronger than in the latter; carbon and sulphur burning in oxygen produce vapours of still greater density, namely, carbon dioxide and sulphur dioxide, and their combustion gives a still brighter light; lastly, phosphorus, which has a very dense vapour, and likewise yields a product of great vapour-density, burns in oxygen with a brilliancy which the eye can scarcely endure. Moreover, the luminosity of a flame is increased by condensing the surrounding gaseous atmosphere, and diminished by rarefying it. The flame of arsenic burning in oxygen may be rendered quite feeble by rarefying the oxygen; and, on the contrary, the faint flame of an ordinary spirit-lamp becomes very bright when placed under the receiver of a condensing-pump. Frankland has also found that candles give much less light when burning on the top of Mont Blanc than in the valley below, although the rate of combustion in the two cases is nearly the same. The effect of condensation in increasing the brightness of a flame is also strikingly seen in the combustion of a mixture of oxygen and hydrogen, which gives but a feeble light when burnt under the ordinary atmospheric pressure, as in the oxy-hydrogen blow-pipe, but a very bright flash when exploded in the Cavendish eudiometer (p. 139), in which the water-vapour produced by the combustion is prevented from expanding.

Flames burning in the air, and not supplied with oxygen from another source, are, as already stated, hollow, the chemical action being necessarily confined to the spot where the two bodies unite. That of a lamp or candle, when carefully examined, is seen to consist of three separate portions. The dark central part, easily rendered evident by depressing upon the flame a piece of fine wire-gauze, consists of combustible matter drawn up by the capillarity of the wick, and volatilised by the heat. This is surrounded by a highly luminous cone or envelope, which, in contact with a cold body, deposits soot. On the outside, a second cone is to be traced, feeble in its light-giving power, but having an exceedingly high temperature. The most probable explanation of these appearances is as follows:—Carbon and hydrogen are very unequal in their attraction for oxygen, the latter greatly exceeding the former in this respect: consequently, when both are present, and the supply of oxygen is limited, the hydrogen takes up the greater portion of the oxygen, to the exclusion of a great part of the carbon. Now, this happens, in the case under consideration, at some little distance within the outer surface of the flame—namely, in the luminous portion; the little oxygen which has penetrated thus far inwards is mostly consumed by the hydrogen, and hydro-carbons are separated, rich in carbon and of great density in the state of vapour (naphthalene, chrysene, pyrene, &c.). These hydro-carbons, which would form smoke if they were cooler, and are deposited on a cold body held in the flame in the form of soot,* become intensely ignited by

Fig. 107.



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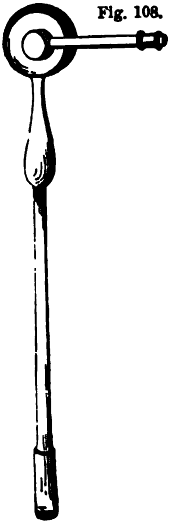
* Soot is not pure carbon, but a mixture of heavy hydro-carbons.

the burning hydrogen, and evolve a light whose whiteness marks a very elevated temperature. In the exterior and scarcely visible cone, these hydro-carbons undergo combustion.

A jet of coal-gas exhibits the same phenomena; but, if the gas be previously mingled with air, or if air be forcibly mixed with, or driven into, the flame, no such separation of carbon occurs; the hydrogen and carbon burn together, forming vapours of much lower density, and the illuminating power almost disappears.

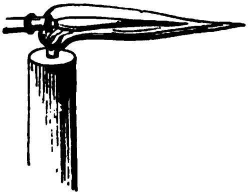
Fig. 108.



The common mouth blow-pipe is an instrument of great utility; it is merely a brass tube fitted with an ivory mouth-piece and terminated by a jet having a small aperture, by which a current of air is driven across the flame of a candle. The best form is perhaps that contrived by Mr. Pepys, and shown in fig. 108. The flame so produced is very peculiar.

Instead of the double envelope just described, two long pointed cones are observed (fig. 109), which, when the blow-pipe is good, and the aperture smooth and round, are very well defined, the outer cone being yellowish, and the inner blue. A double combustion is, in fact going on, by the blast in the inside, and by the external air. The space between the inner and outer cones is filled with exceedingly hot combustible matter, possessing strong reducing or deoxidising powers; while the highly heated air just beyond the point of the exterior cone oxidises with great facility. A small portion of matter, supported on a piece of charcoal, or fixed in a ring at the end of a fine platinum wire, can thus in an instant be exposed to a very high degree of heat under these contrasted circumstances, and observations of great value made in a very short time. The use of the instrument requires an even and uninterrupted blast of some duration, by a method easily acquired with a little patience: it consists in employing for the purpose the muscles of the cheeks alone, respiration being conducted through the nostrils, and the mouth from time to time replenished with air, without intermission of the blast.

Fig. 109.



The Argand lamp, adapted to burn either oil or spirit, but especially the latter, is a very useful piece of chemical apparatus. In this lamp the wick is cylindrical, the flame being supplied with air both inside and outside: the combustion is greatly aided by the chimney, which is made of copper when the lamp is used as a source of heat.

Fig. 110 exhibits, in section, an excellent lamp of this kind for burning alcohol or wood-spirit. It is constructed of thin copper, and furnished with ground caps to the wick-holder and aperture,* by which the spirit is introduced, in order to prevent loss when the lamp is not in use. Glass spirit-lamps (fig. 111), fitted with caps to prevent evaporation, are very convenient for occasional use, being always ready and in order.

Fig. 110.

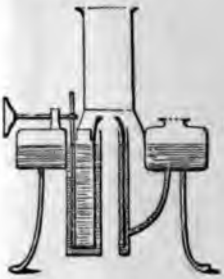
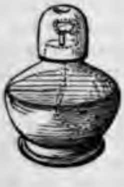
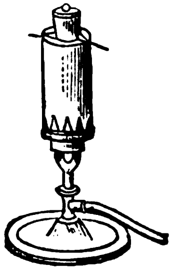


Fig. 111.



In London, and other large towns where coal-gas is to be had, it is constantly used with the greatest economy and advantage in every respect as a source of heat. Retorts, flasks, capsules, and other vessels, can be thus exposed to an easily regulated and invariable temperature for many successive hours. Small platinum crucibles may be ignited to redness by placing them over the flame on a little wire triangle. The arrangement shown in fig. 112, consisting of a common Argand gas-burner fixed on a heavy and low foot, and connected with a flexible tube of caoutchouc or other material, is very convenient.

Fig. 112.



A higher temperature, and perfectly smokeless flame, is, however, obtained by burning the gas previously mixed with air. Such a flame is easily produced by placing a cap of wire-gauze on the chimney of the Argand burner just described, and setting fire to the gas above the wire-gauze. The flame does not penetrate below, but the gas, in passing up the chimney, becomes mixed with air, and this mixture burns above the cap with a blue, smokeless flame.

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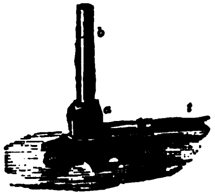
* When in use, this aperture must always be open, otherwise an accident is sure to happen; the heat expands the air in the lamp, and the spirit is forced out in a state of inflammation.

Another kind of burner for producing a smokeless flame has been contrived by Professor Bunsen, and is now very generally used in chemical laboratories. In this burner (fig. 113) the gas, supplied by a flexible tube *t*, passes through a set of small holes into the box at *a*, in which it mixes with atmospheric air entering freely by a number of holes near the top of the box. The gaseous mixture passes up the tube *b*, and is inflamed at the top, where it burns with a tall, blue, smokeless flame, giving very little light, but much heat. By arranging two or more such tubes, together with an air-box containing a sufficient number of holes, a very powerful burner may be constructed.

Fig. 113.



Considerable improvements in this form of burner have been made by Mr. Griffin, who has also constructed, on the same principle, powerful gas-furnaces, affording heat sufficient for the decomposition of silicates, and the fusion of considerable quantities of copper or iron.* The principle of burning a mixture of gas and air is also applied in Hofmann's gas-furnace for organic analysis, which will be described under Organic Chemistry.

The kindling-point, or temperature at which combustion commences, is very different with different substances; phosphorus will sometimes take fire in the hand; sulphur requires a temperature exceeding that of boiling water; charcoal must be heated to redness. Among gaseous bodies the same fact is observed; hydrogen is inflamed by a red-hot wire; light carburetted hydrogen requires a white heat to effect the same thing. When flame is cooled by any means below the temperature at which the rapid oxidation of the combustible gas occurs, it is at once extinguished. Upon this depends the principle of Sir H. Davy's invaluable safety-lamp.

Mention has already been made of the frequent disengagement of great quantities of light carburetted hydrogen gas in coal mines. This gas, mixed with seven or eight times its volume of atmospheric air, becomes highly explosive, taking fire at a light and burning with a pale-blue flame; and many fearful accidents have occurred from the ignition of large quantities of mixed gas and air occupying the extensive galleries and workings of a mine. Davy undertook an investigation with a view to discover some remedy for this constantly occurring calamity; his labours resulted in some exceedingly important discoveries respecting flame, which led to the construction of the lamp which bears his name.

When two vessels filled with a gaseous explosive mixture are connected by a narrow tube, and the contents of one fired by the electric spark, or otherwise, the flame is not communicated to the other, provided the diameter of the tube, its length, and the conducting power for heat of its material, bear a certain proportion to each other; the flame is extinguished by cooling, and its transmission rendered impossible.

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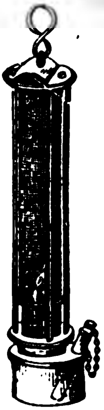
* See the article on Gas-burners and Furnaces in Watts's Dictionary of Chemistry, ii. 782.

In this experiment, high conducting power and diminished diameter compensate for diminution in length; and to such an extent can this be carried, that metallic gauze, which may be looked upon as a series of very short square tubes arranged side by side, when of sufficient degree of fineness, arrests in the most complete manner the passage of flame in explosive mixtures. Now the fire-damp mixture has an exceedingly high kindling point; a red heat does not cause inflammation; consequently, the gauze will be safe for this substance, when flame would pass in almost any other case.

Fig. 114.



The miner's safety-lamp is merely an ordinary oil-lamp, the flame of which is enclosed in a cage of wire-gauze, made double at the upper part, containing about 400 apertures to the square inch. The tube for supplying oil to the reservoir reaches nearly to the bottom of the latter, while the wick admits of being trimmed by a bent wire passing with friction through a small tube in the body of the lamp; the flame can thus be kept burning for any length of time, without the necessity of unscrewing the cage. When this lamp is taken into an explosive atmosphere, although the fire-damp may burn within the cage with such energy as sometimes to heat the metallic tissue to dull redness, the flame is not communicated to the mixture on the outside.

These effects may be conveniently studied by suspending the lamp in a large glass jar, and gradually admitting coal-gas below. The oil-flame is at first elongated, and then, as the proportion of gas increases, extinguished, while the interior of the gauze cylinder becomes filled with the burning mixture of gas and air. As the atmosphere becomes purer, the wick is once more relighted. These appearances are so remarkable that the lamp becomes an admirable indicator of the state of the air in different parts of the mine.*

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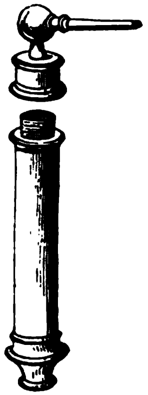
* This is the true use of the lamp, namely, to permit the viewer or superintendent, without risk to himself, to examine the state of the air in every part of the mine; not to enable workman to continue their labours in an atmosphere habitually explosive, which must be unfit for human respiration, although the evil effects may be slow to appear. Owners of coal-mines should be compelled either to adopt efficient means of ventilation, or to close workings of this dangerous character altogether.

The same principle is ingeniously applied in the construction of Hemming's oxyhydrogen safety-jet already mentioned. This is a tube of brass about four inches long, filled with straight pieces of fine brass wire, the whole being tightly wedged together by a pointed rod, forcibly driven into the centre of the bundle. The arrangement thus presents a series of metallic tubes, very long in proportion to their diameter, the cooling powers of which are so great as to prevent the possibility of the passage of flame, even with oxygen and hydrogen. The jet may be used, as before mentioned, with a common bladder, without the chance of explosion. The fundamental fact of flame being extinguished by contact with a cold body, may be strikingly shown by twisting a copper wire into a short spiral, about 0·1 inch in diameter, and then passing it *cold* over the flame of a wax candle; the latter is extinguished. If the spiral be now heated to redness by a spirit-lamp, and the experiment repeated, no such effect follows.

Fig. 115.



Compound of Carbon and Nitrogen. Cyanogen.

When a stream of air is passed over a mixture of charcoal and potassium carbonate kept at a bright red heat, the nitrogen of the air unites with the carbon and the potassium, forming a compound called potassium cyanide, containing 39 parts of potassium, 12 of carbon, and 14 of nitrogen, and represented by the formula KCN. It is a crystalline salt, which dissolves easily in water, and decomposes mercuric oxide, forming potassium hydrate and mercuric cyanide:

$$\begin{array}{ccccccccc} 2KCN & + & H_2O & + & HgO & = & 2KHO & + & HgC_2N_2 \\ \text{Potassium cyanide.} & & \text{Water.} & & \text{Mercuric oxide.} & & \text{Potassium hydroxide.} & & \text{Mercuric cyanide.} \end{array}$$

Now, when dry mercuric cyanide, which is a white crystalline substance, is strongly heated in a glass tube, fitted up like that used for the evolution of oxygen from mercuric oxide (p. 117), it splits up, like the oxide, into metallic mercury, and a gaseous body called cyanogen, containing 12 parts by weight of carbon and 14 of nitrogen, and represented by the formula CN. It must be collected over mercury, as it is rapidly absorbed by water.

Cyanogen is a colourless gas, having a pungent and very peculiar odour, remotely resembling that of peach-kernels. Exposed while at the temperature of 45° F. (7·2° C.) to a pressure of 3·6 atmospheres, it condenses to a thin, colourless, transparent liquid. It is inflammable, and burns with a beautiful purple or peach-blossom-coloured flame, generating carbon dioxide and liberating nitrogen. Its specific gravity is 1·801 referred to air, or 26 referred to hydrogen as unity. One volume of it exploded with 2 vols. oxygen, yields 1 vol. nitrogen and 2 vols. carbon dioxide. Now, the weights of equal volumes of cyanogen, nitrogen, and carbon dioxide are as 26 : 14 : 22. Consequently, 26 parts by weight of cyanogen yield by combustion 14 parts of nitrogen and 44 parts of carbon dioxide, containing 12 parts of carbon; or 26 cyanogen = 12 carbon + 14 nitrogen.

Water dissolves 4 or 5 times its volume of cyanogen gas, and alcohol a much larger quantity: the solution rapidly decomposes, yielding ammonium oxalate, a brown insoluble matter, and other products.

Cyanogen unites (though not directly) with hydrogen, forming the very poisonous compound called hydrocyanic or prussic acid; and with metals, forming compounds called cyanides, analogous in composition and character to the chlorides, iodides, bromides, &c. In short, this group of elements, represented by the formula CN, combines with elementary bodies, and is capable of passing from one state of combination to another, just as if it were itself an elementary body. Such a group of elements is called a compound radicle. We have already had occasion to notice another such group, viz., ammonium, NH_4. Cyanogen, however, is analogous in its chemical relations to the non-metallic elements, chlorine, bromine, oxygen, &c.; whereas ammonium is a quasi-metal analogous to potassium, &c.

The compounds of cyanogen will be further considered under Organic Chemistry.

CHLORINE.

Atomic weight, 35·5. Symbol, Cl.

THIS substance is a member of a very important natural group, containing also iodine, bromine, and fluorine. So great a degree of resemblance exists between these bodies in all their chemical relations, especially between chlorine, bromine, and iodine, that the history of one will almost serve, with a few little alterations, for that of the rest. On account of the occurrence of chlorine, bromine, and iodine in sea-water, the elements of this group are called halogen-elements, and their metallic compounds, haloid compounds.*

Chlorine is a very abundant substance: in common salt it exists in combination with sodium. It is most easily prepared by pouring strong hydrochloric acid upon finely powdered black oxide of manganese (MnO_2) contained in a retort or flask (fig. 116), and applying a gentle heat; a heavy yellow gas is disengaged, which is the substance in question.

It may be collected over warm water, or by displacement: the mercurial trough cannot be employed, as the chlorine rapidly acts upon the metal, and becomes absorbed.

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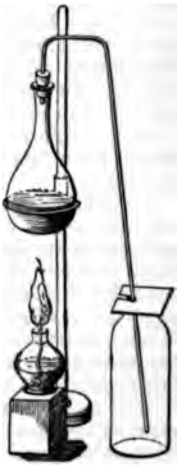
* From ἅλς, the sea.

The reaction consists in an interchange between the 2 atoms of oxygen of the manganese dioxide and 4 atoms of chlorine from the hydrochloric acid, the oxygen uniting with the hydrogen to form water, while, of the chlorine, one-half unites with the manganese, forming a chloride, $MnCl_2$, and the other half is given off as gas:

$$MnO_2 + 4HCl = 2H_2O + MnCl_2 + Cl_2.$$

The same process is used for the preparation of chlorine on the manufacturing scale, the hydrochloric acid which is evolved in large quantities by heating common salt with sulphuric acid, in Leblanc's soda-process being utilised for the purpose.

Fig. 116.



The waste-liquor obtained in the chlorine manufacture consists of an impure solution of manganous chloride $MnCl_2$, from which the manganese may be separated by an alkali in the form of manganous oxide, MnO. But to render the manganese thus precipitated again available for the production of chlorine, it must first be brought to the state of dioxide, and this may be effected by mixing the manganese liquor with an excess of hot milk of lime, or magnesia, and blowing hot air through the mixture. By this means, a compound of manganese dioxide with lime or magnesia, *e.g.* $CaO.MnO_2$, or $CaMnO_3$, called calcium or magnesium manganite, is formed, which, when heated with hydrochloric acid, gives off chlorine in the manner above described. This is Weldon's process for the regeneration of manganese, which is now largely used both in England and on the Continent.

A process for the separation of chlorine from hydrochloric acid, without the use of any manganese compound, has been introduced by Mr. H. Deacon. It consists in passing a mixture of hydrochloric acid gas and oxygen, or air, over cupric sulphate or other cupric salt heated to 370–400° C. (698–752° F.), the hydrochloric acid being then decomposed, its hydrogen combining with the oxygen, and the chlorine being set free. The best way of conducting the process is to pass the mixed gases over pieces of brick soaked in solution of cupric sulphate and dried. The action of the copper salt is not well understood, but appears to belong to that class of phenomena called catalytic or contact actions. Other metallic salts act in a similar way, but less completely.

Chlorine is a yellow gaseous body, of intolerably suffocating properties, producing very violent cough and irritation when inhaled, even in exceedingly small quantity. It is soluble to a considerable

gravity of 2·47;
[illegible] grams; exposed to a pressure of about
condenses to a yellow limpid liquid.

Chlorine has but little attraction for oxyger
principally exerted towards hydrogen and the
taper plunged into the gas continues to burn w
and emits a large quantity of smoke, the hydrog
alone consumed, and the carbon separated. If
wetted with oil of turpentine, and thrust into a
chlorine, the chemical action of the latter upon
violent as to cause inflammation, accompanied b
of soot. Chlorine may, by indirect means, be ma
carbon; but this combination never occurs under
described.

Phosphorus takes fire spontaneously in chlorin
pale and feebly luminous flame. Several of the
leaf, powdered antimony, and arsenic, undergo c
same manner. A mixture of equal measures of chlo
explodes with violence on the passage of an electri
application of a lighted taper, hydrochloric acid g
Such a mixture may be kept in the dark for any len
out change: exposed to diffuse daylight, the two g
while the direct rays of the sun induce instantaneo

The most characteristic property of chlorine
power; the most stable organic colouring princip
decomposed and destroyed by this remarkable ag
example, which resists the action of strong oil of vit
by chlorine into a brownish substance, to which
cannot be restored. The presence of water is e
changes, for the gas in a state of perfect dryness i
of affecting litmus.

Chlorine is largely

absence of bleaching-powder, either of the methods for the production of the gas described may be had recourse to, always taking care to avoid an excess of acid.

Hydrogen Chloride, or **Hydrochloric Acid,** HCl; also called *Chlorhydric* and *Muriatic Acid.*—This substance, in a state of solution in water, has long been known. The gas is prepared with the utmost ease by heating, in a flask fitted with a cork and bent tube, a mixture of common salt and oil of vitriol diluted with a small quantity of water; it must be collected by displacement, or over mercury. It is a colourless gas, which fumes strongly in the air from condensing the atmospheric moisture; it has an acid, suffocating odour, but is much less offensive than chlorine. Exposed to a pressure of 40 atmospheres, it liquefies.

Hydrochloric acid gas has a density of 1·269 compared with air, or 18·25 compared with hydrogen as unity. It is exceedingly soluble in water, that liquid taking up, at the temperature of the air, about 418 times its bulk. The gas and solution are powerfully acid.

The action of sulphuric acid on common salt, or any analogous substance, is explained by the equation,

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

The composition of hydrochloric acid may be determined by synthesis: when a measure of chlorine and a measure of hydrogen are fired by the electric spark, two measures of hydrochloric acid gas result, the combination being unattended by change of volume. By weight it contains 35·5 parts of chlorine and 1 part of hydrogen.

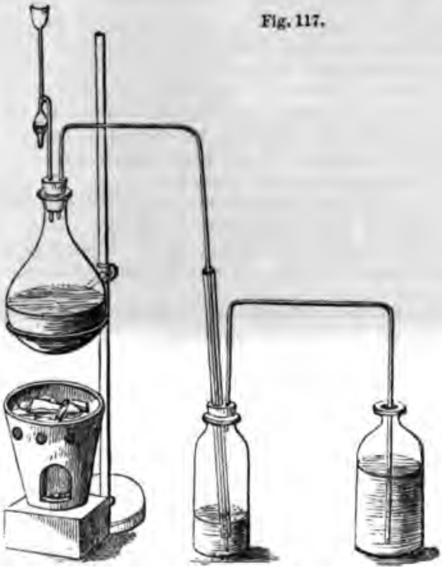
Solution of hydrochloric acid, the liquid acid of commerce, is a very important preparation, and of extensive use in chemical pursuits: it is best prepared by the following arrangement:—

A large glass flask, containing a quantity of common salt, is fitted with a cork and bent tube, in the manner represented in fig. 117: this tube passes through and below a second tube into a wide-necked bottle, containing a little water, into which the open tube dips. A bent tube is adapted to another hole in the cork of the wash-bottle, so as to convey the purified gas into a quantity of distilled water, by which it is instantly absorbed: the joints are made air-tight by melting a little yellow wax over the corks.

A quantity of sulphuric acid, about equal in weight to the salt, is then slowly introduced by the funnel; the disengaged gas is at first wholly absorbed by the water in the wash-bottle, but when this becomes saturated, it passes into the second vessel, and there dissolves. When all the acid has been added, heat may be applied to the flask by a charcoal chauffer, until its contents appear nearly dry, and the evolution of gas almost ceases, when the process may be stopped. As much heat is given out during the condensation of the gas, it is necessary to surround the condensing vessel with cold water.

The simple wash-bottle, shown in figure 117, will be found an exceeding usefully contrivance in a great number of chemical operations. It serves in the present, and in many similar cases to retain any liquid or solid matter mechanically carried over with the gas, and it may be always employed when a gas of any kind is to be passed through an alkaline or other solution. The open tube dipping into the liquid prevents the possibility of absorption, by which a partial vacuum would be occasioned, and the liquid of the second vessel lost by being driven into the first.

Fig. 117.



The arrangement by which the acid is introduced also deserves a moment's notice (fig. 118). The tube is bent twice upon itself, and a bulb blown in one portion: the liquid poured into the funnel rises upon the opposite side of the first bend until it reaches the second; it then flows over and runs into the flask. Any quantity can then be got into the latter without the introduction of air, and without the escape of gas from the interior. The funnel acts also as a kind of safety-valve, and in both directions; for if by any chance the delivery-tube should be stopped, and the issue of gas prevented, its increased elastic force soon drives the little column of liquid out of the tube, the gas escapes, and the vessel is saved. On the other hand, any absorption within is quickly compensated by the entrance of air through the liquid in the bulb.

The plan employed on the large scale by the manufacturer is the same in principle as that described; he merely substitutes a large iron cylinder, or apparatus made of lead, for the flask, and vessels of stoneware for those of glass.

Fig. 118.

Pure solution of hydrochloric acid is transparent and colourless: when strong it fumes in the air by evolving a little gas. It leaves no residue on evaporation, and gives no precipitate or opacity with diluted solution of barium chloride. When saturated with the gas, it has a specific gravity of 1·21, and contains about 42 per cent. of real acid. The commercial acid, which is obtained in immense quantity as a secondary product in the manufacture of sodium sulphate by the action of sulphuric acid upon common salt, has usually a yellow colour, and is very impure, containing salts, sulphuric acid, chloride of iron, and organic matter. It may be rendered sufficiently pure for most purposes by diluting it to the density of 1·1, which happens when the strong acid is mixed with its own bulk or rather less of water, and then distilling it in a retort furnished with a Liebig's condenser.

On distilling an aqueous solution of hydrochloric acid, an acid is produced boiling at 110° which contains 20·22 per cent. of anhydrous hydrochloric acid: a more concentrated solution when heated gives off hydrochloric acid gas; a weaker solution loses water. Roscoe and Dittmar have proved that the composition of the distillate varies with the atmospheric pressure; it cannot, therefore, be viewed as a chemical compound.

A crystalline hydrate of hydrochloric acid, having the composition $HCl . 2H_2O$, is formed by passing a stream of nearly dry hydrochloric acid gas through the concentrated aqueous acid cooled by a freezing mixture to $-22°$. The crystals decompose rapidly in the air, emitting white fumes; they dissolve very quickly in water at ordinary temperatures; very slowly at $-18°$.

Mixtures of snow and hydrochloric acid form very powerful and economical refrigerants. With two parts of snow and 1 part of the acid a lowering of temperature to $-32°$ is readily obtained.*

Nitro-hydrochloric Acid.—A mixture of nitric and hydrochloric acid has long been known under the name of *aqua regia*, from its property of dissolving gold. When these two substances are heated together, they both undergo decomposition, nitrogen tetroxide and chlorine being evolved. This, at least, appears to be the final result of the action: at a certain stage, however, two peculiar substances, consisting of nitrogen, oxygen, and chlorine (chloronitric acid gas, $NOCl_2$, and chloronitrous gas, $NOCl$), appear to be formed. It is only the chlorine which attacks the metal.

The presence of hydrochloric acid, or any other soluble chloride, is easily detected by solution of silver nitrate. A white curdy precipitate is produced, insoluble in nitric acid, freely soluble in ammonia, and subject to blacken by exposure to light.

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* Pierre and Puchot, Comptes rendus, lxxxii. 45.

Oxides and Oxyacids of Chlorine.

There are four oxyacids of chlorine, which may be regarded as oxides of hydrochloric acid; thus—

		Composition by weight.				
	Formula.	Hydrogen.		Chlorine.		Oxygen.
Hydrochloric acid,	HCl	1	+	35·5		
Hypochlorous acid,	$HClO$	1	+	35·5	+	16
Chlorous acid, .	$HClO_2$	1	+	35·5	+	32
Chloric acid, .	$HClO_3$	1	+	35·5	+	48
Perchloric acid,	$HClO_4$	1	+	35·5	+	64

The anhydrous chlorine oxides corresponding with hypochlorous and chlorous acids are also known, namely—

	Chlorine.		Chlorine.		Oxygen.
Chlorine monoxide, or Hypochlorous oxide, Cl_2O, . .	35·5	+	35·5	+	16
Chlorine trioxide, or Chlorous oxide, Cl_2O_3, ...	35·5	+	35·5	+	48

Also an oxide to which there is no corresponding acid, namely—

	Chlorine.		Oxygen.
Chlorine tetroxide, Cl_2O_4 . .	2 × 35·5	+	64

The oxides corresponding with chloric and perchloric acid have not been obtained.

Hypochlorous and chloric acids are produced by the action of chlorine on certain metallic oxides in presence of water; hypochlorous and chlorous acids also by direct oxidation of hydrochloric acid. Perchloric acid and chlorine tetroxide result from the decomposition of chloric acid.

Hypochlorous Oxide, Acid, and **Salts.**—The oxide is best prepared by the action of chlorine gas upon dry mercuric oxide. This oxide, prepared by precipitation, and dried by exposure to a strong heat, is introduced into a glass tube kept cool, and well-washed dry chlorine gas is slowly passed over it. Mercuric chloride ($HgCl_2$) and hypochlorous oxide are thereby formed; the latter is collected by displacement. The reaction by which it is produced is represented by the equation,

$$2HgO + Cl_4 = Cl_2O + HgCl_2.$$

The mercuric chloride, however, does not remain as such; it combines with another portion of the oxide when the latter is in excess, forming a peculiar brown compound, an oxychloride of mercury $HgCl_2.HgO$. It is remarkable that the *crystalline* mercuric oxide prepared by calcining the nitrate, or by the direct oxidation of the metal, is scarcely acted upon by chlorine under the circumstances described.

Hypochlorous oxide is a pale-yellow gaseous body, containing, in every two measures, two measures of chlorine and one of oxygen, and is therefore analogous in constitution to water. It explodes, although with no great violence, by slight elevation of temperature. Its odour is peculiar, and quite different from that of chlorine. When the flask or bottle in which the gas is received is exposed to artificial cold by the aid of a mixture of ice and salt, the hypochlorous oxide condenses to a deep-red liquid, slowly soluble in water, and very subject to explosion.

Hypochlorous acid is produced by the solution of hypochlorous oxide in water: also by passing air saturated with hydrochloric acid gas through a solution of potassium permanganate acidulated with hydrochloric acid and heated in a water-bath: the distillate is a solution of hypochlorous acid, formed by oxidation of the hydrochloric acid; thirdly, by decomposing a metallic hypochlorite with sulphuric acid or other oxacid; fourthly, by passing chlorine gas into water holding in suspension a solution containing metallic oxides, hydroxides, carbonates, sulphates, phosphates, &c., the most advantageous for the purpose being mercuric oxide, or calcium carbonate (chalk), $CaCO_3$, the products in this case being carbon dioxide, calcium chloride, and hypochlorous acid:

$$CaCO_3 + H_2O + Cl_4 = CO_2 + CaCl_2 + 2HClO\,.$$

The aqueous solution of hypochlorous acid has a yellowish colour, an acid taste, and a characteristic sweetish smell. The strong acid decomposes rapidly even when kept in ice. The dilute acid is more stable, but is decomposed by long boiling into chloric acid, water, chlorine, and oxygen. Hydrochloric acid decomposes it, with formation of chlorine:

$$HClO + HCl = H_2O + Cl_2\,.$$

It is a very powerful bleaching and oxidising agent, converting many of the elements—iodine, selenium, and arsenic, for example—into their highest oxides, and at the same time liberating chlorine.

Metallic hypochlorites may be obtained in the pure state by neutralising hypochlorous acid with metallic hydroxides, such as those of sodium, calcium, copper, &c.; but they are usually prepared by passing chlorine gas into solutions of alkalis or alkaline carbonates, or over the dry hydroxides of the earth-metals. In this process a metallic chloride is formed at the same time. With dry slaked lime, for example, which is a hydroxide of calcium, CaH_2O_2, the products are calcium hypochlorite, $CaCl_2O_2$, calcium chloride, and water:

$$2CaH_2O_2 + Cl_4 = CaCl_2O_2 + CaCl_2 + 2H_2O\,.$$

The salts thus obtained constitute the bleaching and disinfecting salts of commerce. They will be more fully described under the head of Calcium Salts.

Chlorous Oxide, Acid, and Salts.—The oxide is prepared by heating in a flask filled to the neck, a mixture of four parts of potassium chlorate and 3 parts of arsenious oxide with 12 parts of nitric acid previously diluted with 4 parts of water. During the operation, which must be performed in a water-bath, a greenish-yellow gas is evolved, which is permanent in a freezing mixture of ice and salt, but liquefiable by extreme cold. It dissolves freely in water and in alkaline solutions, forming chlorous acid and metallic chlorites. The reaction by which chlorous oxide is formed is somewhat complicated. The arsenious oxide deprives the nitric acid of part of its oxygen, reducing it to nitrous acid, which is then reoxidised at the expense of the chloric acid, reducing it to chlorous oxide:

$$\underset{\text{Chloric acid.}}{2HClO_3} + \underset{\text{Nitrous acid.}}{2HNO_2} = \underset{\text{Nitric acid.}}{2HNO_3} + H_2O + \underset{\text{Chlorous oxide.}}{Cl_2O_3}.$$

Chlorous Acid may be prepared by condensing chlorous oxide in water, or by decomposing a metallic chlorite with dilute sulphuric or phosphoric acid. Its concentrated solution is a greenish-yellow liquid having strong bleaching and oxidising properties. It does not decompose carbonates, but acts strongly with caustic alkalis and earths to form chlorites.

Chlorine Tetroxide, Cl_2O_4.—When potassium chlorate is made into a paste with concentrated sulphuric acid, and cooled, and this paste is very cautiously heated by warm water in a small glass retort, a deep yellow gas is evolved, which is the body in question; it can be collected only by displacement, since mercury decomposes and water absorbs it.

Chlorine tetroxide has a powerful odour, quite different from that of the preceding compounds, and of chlorine itself. It is exceedingly explosive, being resolved with violence into its elements by a temperature short of the boiling point of water. Its preparation is, therefore, always attended with danger, and should be performed only on a small scale. It is composed by measure of one volume of chlorine and two volumes of oxygen, condensed into two volumes. It may be liquefied by cold. The solution of the gas in water bleaches.

The *euchlorine* of Davy, prepared by gently heating potassium chlorate with dilute hydrochloric acid, is probably a mixture of chlorine tetroxide and free chlorine.

The production of chlorine tetroxide from potassium chlorate and sulphuric acid depends upon the spontaneous splitting of the chloric acid into chlorine tetroxide and perchloric acid, which latter remains as a potassium salt.

$$\underset{\text{Potassium chlorate.}}{6KClO_3} + \underset{\text{Hydrogen sulphate.}}{3H_2SO_4} = 2Cl_2O_4 + \underset{\text{Hydrogen perchlorate.}}{2HClO_4} + \underset{\text{Potassium sulphate.}}{3K_2SO_4} + 2H_2O.$$

When a mixture of potassium chlorate and sugar is touched with a drop of oil of vitriol, it is instantly set on fire, the chlorine tetroxide disengaged being decomposed by the combustible substance with such violence as to cause inflammation. If crystals of potassium chlorate be thrown into a glass of water, a few small fragments of phosphorus added, and then oil of vitriol poured down a narrow funnel reaching to the bottom of the glass, the phosphorus will burn beneath the surface of the water, by the assistance of the oxygen of the chlorine tetroxide disengaged. The liquid at the same time becomes yellow, and acquires the odour of that gas.

Chloric Acid, $HClO_3$.—This is the most important compound of the series. When chlorine is passed to saturation into a moderately strong hot solution of potassium hydroxide or carbonate, and the liquid concentrated by evaporation, it yields, on cooling, flat tabular crystals of a colourless salt, consisting of potassium chlorate. The mother-liquor contains potassium chloride:

$$\underset{\text{Potassium oxide.}}{3K_2O} + Cl_6 = \underset{\text{Potassium chloride.}}{5KCl} + \underset{\text{Potassium chlorate.}}{KClO_3}$$

From potassium chlorate, chloric acid may be obtained by boiling the salt with a solution of hydrofluosilicic acid, which forms an almost insoluble potassium salt, decanting the clear liquid, and digesting it with a little silica, which removes the excess of the hydrofluosilicic acid. Filtration through paper must be avoided.

By cautious evaporation, the acid may be so far concentrated as to assume a syrupy consistence; it is then very easily decomposed. It sometimes sets fire to paper, or other dry organic matter, in consequence of the facility with which it is deoxidised by combustible bodies.

The chlorates are easily recognised; they give no precipitate when in solution with silver nitrate; they evolve pure oxygen when heated, passing thereby into chlorides; and they afford, when treated with sulphuric acid, the characteristic explosive yellow gas already described. The dilute solution of the acid has no bleaching power.

Perchloric Acid, $HClO_4$.—When powdered potassium chlorate is thrown by small portions at a time into hot nitric acid, a change takes place of the same description as that which happens when sulphuric acid is used, but with this important difference, that the chlorine and oxygen, instead of being evolved in a dangerous state of combination, are emitted in a state of *mixture*. The result of the action is a mixture of potassium nitrate and perchlorate, which may be readily separated by their difference of solubility.

Perchloric acid is obtained by distilling potassium perchlorate with sulphuric acid. Pure perchloric acid is a colourless liquid, of 1·782 sp. gr. at 15·5°, not solidifying at − 35°; it soon becomes coloured, even if kept in the dark, and after a few weeks decomposes with explosion. The vapour of perchloric acid is transparent and colourless: in contact with moist air, it produces dense white fumes. The acid, when cautiously mixed with a small quantity of water, solidifies to a crystalline mass, which is a compound of perchloric acid with one molecule of water, $HClO_4 + H_2O$. When brought in contact with carbon, ether, or other organic substances, perchloric acid explodes with nearly as much violence as chloride of nitrogen.

Compound of Chlorine and Nitrogen, NCl_3.—When sal-ammoniac or ammonia nitrate is dissolved in water, and a jar of chlorine inverted in the solution, the gas is absorbed, and a deep yellow oily liquid is observed to collect upon the surface of the solution, ultimately sinking in globules to the bottom. This is nitrogen chloride, one of the most dangerously explosive substances known. The following is the safest method of conducting the experiment:—

A somewhat dilute and tepid solution of pure sal-ammoniac in distilled water is poured into a clean basin, and a bottle of chlorine, the neck of which is quite free from grease, inverted in it. A shallow and heavy leaden cup is placed beneath the mouth of the bottle to collect the product. When enough has been obtained, the leaden vessel may be withdrawn with its dangerous contents, the chloride remaining covered with a stratum of water. The operator should protect his face with a strong wire-gauze mask when experimenting upon this substance.

The change may be explained by the equation—

$$NH_4Cl + 6Cl = NCl_3 + 4HCl.$$

Nitrogen chloride is very volatile, and its vapour is exceedingly irritating to the eyes. It has a specific gravity of 1·653. It may be distilled at 71°, although the experiment is attended with great danger. Between 93° and 105° it explodes with the most fearful violence. Contact with almost any combustible matter, as oil or fat of any kind, determines the explosion at common temperatures: a vessel of porcelain, glass, or even of cast-iron, is broken to pieces, and the leaden cup receives a deep indentation. This body has usually been supposed to contain nitrogen and chlorine in the proportion of 14 parts of the former to 106·5 parts of the latter, but recent experiments upon the corresponding iodine compound (p. 201) induce a belief that it contains hydrogen.*

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* Instead of NCl_3, it may in reality be $NHCl_2$, or NH_2Cl.

Chlorine and Carbon.—Several compounds of chlorine and carbon are known, namely, C_2Cl_2, C_2Cl_4, C_2Cl_6, and CCl_4. They are obtained indirectly by the action of chlorine upon certain organic compounds, and will be described under Organic Chemistry.

The *Oxychloride of Carbon*, $COCl_2$, called also *Carbonyl Chloride* and *Phosgene*, has been already mentioned (p. 172).

BROMINE.

Atomic weight, 80. Symbol, Br.

BROMINE* was discovered by Balard in 1826. It is found in sea-water, and is a frequent constituent of saline springs, chiefly as magnesium bromide: a celebrated spring of the kind exists near Kreuznach, in Prussia. Bromine may be obtained pure by the following process, which depends upon the fact that ether, agitated with an aqueous solution of bromine, removes the greater part of that substance.

The mother-liquor, from which the less soluble salts have separated by crystallisation, is exposed to a stream of chlorine, and then shaken up with ether; the chlorine decomposes the magnesium bromide, and the ether dissolves the bromine thus set free. On standing, the ethereal solution, having a fine red colour, separates, and may be removed by a funnel or pipette. Caustic potash is then added in excess, and heat applied; bromide and bromate of potassium are formed. The solution is evaporated to dryness, and the saline matter, after ignition to redness to decompose the bromate, is heated in a small retort with manganese dioxide and sulphuric acid diluted with a little water, the neck of the retort being plunged into cold water. The bromine volatilises in the form of a deep red vapour, which condenses into drops beneath the liquid.

Bromine is at common temperatures a thin red liquid of an exceedingly intense colour, and very volatile; it freezes at about $-24{\cdot}5$ and boils at 63°. The density of the liquid is 2·976, and that of the vapour 5·54 compared with air, and 80 compared with hydrogen. The odour of bromine is very suffocating and offensive, much resembling that of iodine, but more disagreeable. It is slightly soluble in water, more freely in alcohol, and most abundantly in ether. The aqueous solution bleaches.

Hydrogen Bromide, or **Hydrobromic Acid**, HBr.—This substance bears the closest resemblance to hydriodic acid: it has the same constitution by volume, very nearly the same properties, and may be prepared by means exactly similar, substituting the one body for the other (see page 199). The solution of hydrobromic acid has also the power of dissolving a large quantity of bromine, thereby acquiring a red tint. Hydrobromic acid contains by weight 80 parts bromine and 1 part hydrogen.

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* From *βρῶμος*, a noisome smell.

Bromic Acid, $HBrO_3$.—Caustic alkalis in presence of bromine undergo the same change as with chlorine, a metallic bromide and bromate being produced; these may be separated by the inferior solubility of the latter. Bromic acid, obtained from barium bromate, closely resembles chloric acid; it is easily decomposed. The bromates, when heated, lose oxygen and become bromides.

A hypobromous acid corresponding with hypochlorous acid is likewise known.

IODINE.

Atomic weight, 127. Symbol, I.

THIS element was first noticed in 1812 by M. Courtois, of Paris. Minute traces are found in combination with sodium or potassium in sea-water, and occasionally a much larger proportion in that of certain mineral springs. It seems to be in some way beneficial to many marine plants, as these latter have the power of abstracting it from the surrounding water, and accumulating it in their tissues. It is from this source that all the iodine of commerce is derived. It has lately been found in minute quantity in some aluminous slates of Sweden, and in several varieties of coal and turf.

Kelp, or the half-vitrified ashes of sea-weeds, prepared by the inhabitants of the Western Islands and the northern shores of Scotland and Ireland, is treated with water, and the solution filtered. The liquid is then concentrated by evaporation until it is reduced to a very small volume, the sodium chloride, sodium carbonate, potassium chloride, and other salts being removed as they successively crystallise. The dark-brown mother-liquor left contains very nearly the whole of the iodine, as iodide of sodium, magnesium, &c.: this is mixed with sulphuric acid and manganese dioxide, and gently heated in a leaden retort, when the iodine distils over and condenses in the receiver. The theory of the operation is exactly analogous to that of the preparation of chlorine (p. 187); in practice, however, it requires careful management, otherwise the impurities present in the solution interfere with the general result:

$$MnO_2 + 2KI + 2H_2SO_4 = 2H_2O + K_2SO_4 + MnSO_4 + I_2.$$

The manganese is not absolutely necessary: potassium or sodium iodide, heated with an excess of sulphuric acid, evolves iodine. This effect is due to a secondary action between the hydriodic acid first produced and the excess of the sulphuric acid, in which both suffer decomposition, yielding iodine, water, and sulphurous acid.

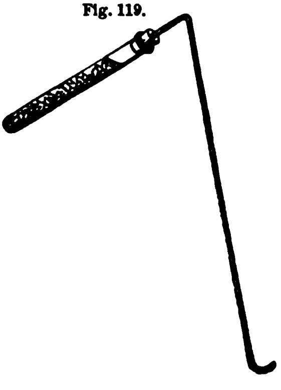
Iodine crystallises in plates or scales of a bluish-black colour and imperfect metallic lustre, resembling that of plumbago: the crystals are sometimes very large and brilliant. Its density is 4·948. It melts at 107°, and boils at 175°, the vapour having an exceedingly beautiful violet colour.* It is slowly volatile, however, at common temperatures, and exhales an odour much resembling that of chlorine. The density of the vapour is 8·716 compared with air, 127 compared with hydrogen. Iodine requires for solution about 7000 parts of water, which nevertheless acquires a brown colour; in alcohol it is much more freely soluble. Solutions of hydriodic acid and the iodides of the alkali-metals also dissolve a large quantity: these solutions are not decomposed by water, which is the case with the alcoholic tincture.

Iodine stains the skin, but not permanently; it has a very energetic action upon the animal system, and is much used in medicine.

One of the most characteristic properties of iodine is the production of a splendid blue colour by contact with starch. The iodine for this purpose must be free or uncombined. It is easy, however, to make the test available for the purpose of recognising the presence of the element in question when a soluble iodide is suspected; it is only necessary to add a very small quantity of chlorine-water, when the iodine, being displaced from combination, becomes capable of acting upon the starch.

Hydrogen Iodide, or **Hydriodic Acid**, HI.—The simplest process for preparing hydriodic acid gas is to introduce into a glass tube, sealed at one extremity, a little iodine, then a small quantity of roughly-powdered glass moistened with water, upon this a few fragments of phosphorus, and lastly more glass, this order of iodine, glass, phosphorus, glass, being repeated until the tube is half or two-thirds filled. A cork and narrow bent tube are then fitted, and gentle heat applied. The gas is best collected by displacement of air. The process depends on the formation of an iodide of phosphorus and its subsequent decomposition by water, whereby hydrogen phosphite, or phosphorous acid, H_3PO_3, and hydrogen iodide are produced: $P_2 + I_6 + 6H_2O = 6HI + 2H_3PO_3$. The glass merely serves to moderate the violence of the action of the iodine upon the phosphorus.

Fig. 119.



Hydriodic acid gas greatly resembles the corresponding chlorine

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[*] Whence the name, from ἰώδης, violet-coloured.

compound; it is colourless, and highly acid; it fumes in the air, and is very soluble in water. Its density is about 4·4 compared with air, 64 compared with hydrogen. By weight, it is composed of 127 parts iodine and 1 part hydrogen; and by measure of equal volumes of iodine vapour and hydrogen united without condensation.

Solution of hydriodic acid may be prepared by a process much less troublesome than the above. Iodine in fine powder is suspended in water, and a stream of washed hydrogen sulphide passed through the mixture; sulphur is deposited, and the iodine converted into hydriodic acid. When the liquid has become colourless, it is heated, to expel the excess of hydrogen sulphide, and filtered. The solution cannot be kept long, especially if it be concentrated; the oxygen of the air gradually decomposes the hydriodic acid, and iodine is set free, which, dissolving in the remainder, communicates to it a brown colour.

Compounds of Iodine and Oxygen.

The most important of these are the iodic and periodic oxides.

		Composition by weight.	
		Iodine.	Oxygen.
Iodic oxide	I_2O_5 . .	$2 \times 127 +$	80
Periodic oxide,	I_2O_7 . .	$2 \times 127 +$	112

Both these are acid oxides, uniting with water and metallic oxides, and forming salts called iodates and periodates.

Hydrogen Iodate, or **Iodic Acid,** $H_2O.I_2O_5$, or HIO_3, may be prepared by the direct oxidation of iodine with nitric acid of specific gravity 1·5. Five parts of dry iodine with 200 parts of nitric acid are kept at a boiling temperature for several hours, or until the iodine has disappeared. The solution is then cautiously distilled to dryness, and the residue dissolved in water and made to crystallise.

Iodic acid is a very soluble substance, crystallising in colourless six-sided tables. At 107° it is resolved into water and iodic oxide, which forms tabular rhombic crystals, and when heated to the temperature of boiling olive oil, is completely resolved into iodine and oxygen. The solution of iodic acid is readily deoxidised by sulphurous acid. The iodates much resemble the chlorates: that of potassium is decomposed by heat into potassium iodide and oxygen gas.

Hydrogen Periodate, or **Periodic Acid,** $H_2O.I_2O_7$, or HIO_4.—When solution of sodium iodate is mixed with caustic soda, and a current of chlorine passed through the liquid, two salts are formed—namely, sodium chloride and a sparingly soluble compound of sodium periodate with sodium hydroxide and water, $NaIO_4.NaHO.H_2O$, or $Na_2H_3IO_6$, the reaction taking place as represented by the equation—

$$NaIO_3 + 3NaHO + Cl_2 = 2NaCl + Na_2H_3IO_6.$$

This sodium salt is separated, converted into a silver-salt, and dissolved in nitric acid: the solution yields, on evaporation, crystals of yellow silver periodate, from which the acid may be separated by the action of water, which resolves the salt into free acid and an insoluble basic periodate.

Periodic acid crystallises from its aqueous solution in deliquescent oblique rhombic prisms, which melt at 130°, and are resolved at 170° into water and a white mass of periodic oxide, which at 180° or 190° gives off oxygen with great rapidity, and leaves iodic oxide.

The solution of periodic acid is reduced by many organic substances, and instantly by hydrochloric acid, sulphurous acid, and hydrogen sulphide. With hydrochloric acid it forms water, iodine chloride, and free chlorine. The metallic periodates are resolved by heat into oxygen and metallic iodide.

Compounds of Iodine and Nitrogen.—When finely powdered iodine is put into caustic ammonia, it is in part dissolved, giving a deep-brown solution, and the residue is converted into a black powder, called nitrogen iodide, NI_3. The brown liquid consists of hydriodic acid holding iodine in solution, and is easily separated from the solid product by a filter. The latter, while still wet, is distributed in small quantities upon separate pieces of bibulous paper, and left to dry in the air.

Nitrogen iodide is a black insoluble powder, which, when dry, explodes with the slightest touch—even that of a feather—and sometimes without any obvious cause. The explosion is, however, not nearly so violent as that of nitrogen chloride, and is attended with the production of violet fumes of iodine. According to Dr. Gladstone, this substance contains hydrogen, and may be viewed as NHI_2, that is, as ammonia in which two-thirds of the hydrogen are replaced by iodine. According to the researches of Bunsen, it must be viewed as a combination of nitrogen tri-iodide with ammonia, $NI_3.NH_3$. It appears, however, that the substance called nitrogen iodide varies in composition. Gladstone, by changing the mode of preparation, obtained several compounds of nitrogen tri-iodide with ammonia.

Compounds of Iodine and Chlorine.—Iodine unites directly with chlorine, forming a monochloride and a trichloride. There is also a tetrachloride produced by spontaneous decomposition of the monochloride.

The *monochloride*, ICl, is obtained by passing dry chlorine over iodine till the whole is liquefied, but no longer; also by distilling iodine with potassium chlorate, oxygen being then evolved, the monochloride distilling over, and a mixture of chloride, iodate, and perchlorate of potassium remaining behind.

$$I_2 + 3KClO_3 = O_2 + ICl + KCl + KIO_3 + KClO_4.$$

Iodine monochloride is a reddish-brown oily liquid, having a suffocating odour and astringent taste; soluble in alcohol and ether; decomposed by water, with formation of hydrochloric and iodic acids, and separation of iodine. It sometimes solidifies in yellow needles. Sulphurous acid and hydrogen sulphide decompose it, with separation of iodine; with aqueous solutions of alkalis, it yields a chloride and an iodate, together with free iodine; thus, with potash—

$$5ICl + 6KHO = 5KCl + KIO_3 + 3H_2O + I_4.$$

The *trichloride*, ICl , is produced by treating iodine at a gentle heat with chlorine in excess. It crystallises in orange-yellow needles; melts at 20° to 25°, giving off chlorine, which it reabsorbs on cooling; acts on most other substances like the monochloride. In contact with a small quantity of water it is partly resolved into an insoluble yellowish body (probably a mixture of the trichloride with iodic oxide), and a solution containing hydrochloric acid and the monochloride—

$$4ICl_3 + 5H_2O = 10HCl + I_2O_5 + 2ICl.$$

A large quantity of water dissolves it, probably without decomposition, or perhaps as a mixture of hydrochloric and iodic acids containing free iodine—

$$5ICl_3 + 9H_2O = 15HCl + 3HIO_3 + I_2.$$

The *tetrachloride*, ICl_4, produced by spontaneous decomposition of the monochloride, $4ICl = ICl_4 + I_3$, crystallises in red octohedrons.

FLUORINE.

Atomic weight, 19. Symbol, F.

THIS element has never been isolated—at least, in a state fit for examination; its properties are consequently in great measure unknown: but from the observations made, it is presumed to be gaseous, and to possess colour, like chlorine. The compounds containing fluorine can be easily decomposed, and the element transferred from one body to another; but its intense chemical energies towards the metals and towards silicium, a component of glass, have hitherto baffled all attempts to obtain it pure in the separate state. As calcium fluoride, it exists in considerable quantities as fluor-spar, a mineral which crystallises in fine cubes of various colours, and in small quantities in many animal substances, such as bones. Several chemists have endeavoured to obtain it by decomposing silver fluoride by means of chlorine in vessels of fluor-spar, but even these experiments have not led to a decisive result.

Hydrogen Fluoride, or **Hydrofluoric Acid,** HF.—When powdered calcium fluoride is heated with concentrated sulphuric acid in a retort of platinum or lead connected with a carefully cooled receiver of the same metal, a very volatile colourless liquid is obtained, which emits copious white and highly suffocating fumes in the air. This is the anhydrous acid, not however quite pure. It may be obtained in a state of perfect purity by distilling hydrogen-potassium fluoride, HF.KF, to redness in a platinum vessel. As thus prepared, it is at ordinary temperatures a colourless, transparent, mobile liquid, having a specific gravity of 0·9879 at 12·8°, extremely volatile, boiling at 19·4°, fuming densely at ordinary temperatures, and absorbing water greedily from the air.* It contains 19 parts by weight of fluorine to 1 part of hydrogen.

When hydrofluoric acid is put into water, it unites with the latter with great violence; the dilute solution attacks glass with great facility. The concentrated acid, dropped upon the skin, occasions deep and malignant ulcers, so that great care is requisite in its management. Hydrofluoric acid contains 19 parts fluorine and 1 part hydrogen.

In a diluted state, this acid is occasionally used in the analysis of siliceous minerals, when alkali is to be estimated; it is employed also for etching on glass, for which purpose the acid may be prepared in vessels of lead, that metal being but slowly attacked under these circumstances. The vapour of the acid is also very advantageously applied to the same purpose in the following manner:—The glass to be engraved is coated with etching-ground or wax, and the design traced in the usual way with a pointed instrument. A shallow basin, made by beating up a piece of sheet-lead, is then prepared, a little powdered fluor-spar placed in it, and enough sulphuric acid added to form with the latter a thin paste. The glass is placed upon the basin, with the waxed side downwards, and gentle heat applied beneath, which speedily disengages the vapour of hydrofluoric acid. In a very few minutes the operation is complete; the glass is then removed, and cleaned by a little warm oil of turpentine. When the experiment is successful, the lines are very clean and smooth.

No combination of fluorine and oxygen has yet been discovered.

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* Gore, Journal of the Chemical Society [2], ii. 368.

SULPHUR.

Atomic weight, 32. Symbol, S.

This is an elementary body of great importance and interest. It is often found in the free state in connection with deposits of gypsum and rock-salt, and in the fissures of volcanic craters. Sicily furnishes a large proportion of the sulphur employed in Europe. Sulphur also occurs abundantly in combination with iron and other metals, and as sulphuric acid, united to lime and magnesia.

Pure sulphur is a pale-yellow brittle solid, of well-known appearance. It melts when heated, and distils over unaltered, if air be excluded. The crystals of sulphur exhibit two distinct and incompatible forms—namely, first, an octohedron with rhombic base (fig 120), which is the figure of native sulphur, and that assumed when sulphur separates from solution at common temperatures, as when a solution of sulphur in carbon bisulphide is exposed to slow evaporation in the air; and, secondly, a lengthened prism having no relation to the preceding; this happens when a mass of sulphur is melted, and, after partial cooling, the crust on the surface is broken, and the fluid portion poured out. Fig. 121 shows the result of such an experiment.

Fig. 120.

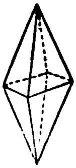
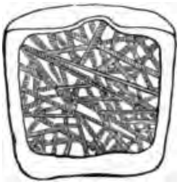


Fig. 121.



The specific gravity of sulphur varies according to the form in which it is crystallised. The octohedral variety has the specific gravity 2·045; the prismatic variety the specific gravity 1·982.

Sulphur melts at 111° (at 114·5°, according to Brodie); at this temperature it is of the colour of amber, and thin and fluid as water; when further heated, it begins to thicken, and to acquire a deeper colour; and between 221° and 249° it is so tenacious that the vessel in which it is contained may be inverted for a moment without the loss of its contents. If in this state it be poured into water, it retains for many hours a remarkably soft and flexible condition, which may be looked upon as the amorphous state of sulphur. After a while it again becomes brittle and crystalline. From the temperature last-mentioned to the boiling-point—about 400°—sulphur again becomes thin and liquid. In the preparation of commercial flowers of sulphur, the vapour is conducted into a large cold chamber, where it condenses in minute crystals. The specific gravity of sulphur vapour is 2·22 referred to that of air as unity, or 32 compared with that of hydrogen (Deville).

Sulphur is insoluble in water and alcohol; oil of turpentine and the fat oils dissolve it, but the best substance for the purpose is carbon bisulphide. In its chemical relations sulphur bears great resemblance to oxygen: to very many oxides there are corresponding sulphides, and the sulphides often unite among themselves, forming crystallisable compounds analogous to oxysalts.

Sulphur is remarkable for the great number of modifications which it is capable of assuming. Of these, however, there are two principal well characterised varieties, one soluble, and the other insoluble in carbon bisulphide, and many minor modifications. The soluble variety is distinguished by Berthelot by the name of *electro-negative sulphur*, because it is the form which appears at the positive pole of the voltaic battery during the decomposition of an aqueous solution of hydrogen sulphide, and is separated from the combinations of sulphur with the electro-positive metals. The insoluble variety is distinguished as *electro-positive sulphur*, because it is the form which appears at the negative pole during the electro-decomposition of sulphurous acid, and separates from compounds of sulphur with the electro-negative elements, chlorine, bromine, oxygen, &c.

The principal modifications of soluble sulphur are the octohedral and prismatic varieties already mentioned, and an amorphous variety which is precipitated as a greenish-white emulsion, known as milk of sulphur, on adding an acid to a dilute solution of an alkaline polysulphide, such, for example, as is obtained by boiling sulphur with milk of lime. This amorphous sulphur changes by keeping into a mass of minute octohedral crystals. Sublimed sulphur appears also to be allied to this modification, but it always contains a small portion of one of the insoluble modifications.

The chief modifications of insoluble sulphur are:—1. The amorphous insoluble variety, obtained as a soft magma by decomposing chlorine bisulphide with water, or by adding dilute hydrochloric acid to the solution of a thiosulphate (p. 212). 2. The plastic sulphur already mentioned as obtained by pouring viscid melted sulphur into water. A very similar variety is produced by boiling metallic sulphides with nitric or nitro-muriatic acid.

When solutions of hydrogen sulphide and ferric chloride are mixed together, a blue precipitate is sometimes formed, which is said to be a peculiar modification of sulphur.

Compounds of Sulphur and Oxygen.

There are two oxides of sulphur, whose names and composition are as follows:—

	Composition by weight.		
	Sulphur.		Oxygen.
Sulphur dioxide or Sulphurous oxide, SO_2 .	32	+	32
Sulphur trioxide or Sulphuric oxide, SO_3 .	32	+	48

Both these oxides unite with water and metallic oxides, or the elements thereof, producing salts; those derived from sulphurous oxide are called sulphites, and those derived from sulphuric acid, sulphates. The composition of the hydrogen salts or acids is as follows:—

	Hydrogen.		Sulphur.		Oxygen.		Water.		Sulphurous oxide.
Hydrogen Sulphite, or Sulphurous acid.	2	+	32	+	48	=	18	+	64
							Water.		Sulphuric oxide.
Hydrogen Sulphate or Sulphuric acid,	2	+	32	+	64	=	18	+	80

The formulæ of these acids are—

Sulphurous acid, $H_2SO_3 = H_2O.SO_2$
Sulphuric acid, $H_2SO_4 = H_2O.SO_3$

The replacement of half or the whole of the hydrogen by metals gives rise to metallic sulphites and sulphates.

By the combination of sulphuric oxide with sulphuric acid in the proportion of SO_3 to H_2SO_4 (or 80 parts by weight of the oxide to 98 of the acid) an acid is formed called disulphuric or pyrosulphuric acid, having the composition $H_2S_2O_7$ or

Hydrogen.		Sulphur.		Oxygen.
2	+	64	+	112

There are also several acids of sulphur, with their corresponding metallic salts, to which there are no corresponding anhydrous oxides, viz.:—

1. *Hyposulphurous Acid*, H_2SO_2, having the composition of sulphurous acid *minus* one atom of oxygen. Its composition by weight is—

Hydrogen.		Sulphur.		Oxygen.
2	+	32	+	32

2. *Thiosulphuric Acid*, $H_2S_2O_3$, having the composition of sulphuric acid in which one-fourth of the oxygen is replaced by sulphur. Its composition by weight is—

Hydrogen.		Sulphur.		Oxygen.
2	+	64	+	48

Closely allied to this acid is—

3. *Seleniosulphuric Acid*, H_2SSeO_3, having the composition of

sulphuric acid in which one-fourth of the oxygen is replaced by selenium. Its composition by weight is—

Hydrogen.		Sulphur.		Selenium.		Oxygen.
2	+	32	+	79·4	+	48

4. A series of acids called *Polythionic Acids*,* in which the same quantities of oxygen and hydrogen are united with quantities of sulphur in the proportion of the numbers 2, 3, 4, 5, viz:—

			Hydrogen.		Sulphur.		Oxygen.
Dithionic, or Hyposulphuric acid,	$H_2S_2O_6$	.	2	+	64	+	96
Trithionic acid, . .	$H_2S_3O_6$	.	2	+	96	+	96
Tetrathionic acid, . .	$H_2S_4O_6$	.	2	+	128	+	96
Pentathionic acid, . .	$H_2S_5O_6$	.	2	+	150	+	96

Sulphur Dioxide, or **Sulphurous Oxide**, SO_2.—This is the only product of the combustion of sulphur in dry air or oxygen gas. It is most conveniently prepared by heating sulphuric acid with metallic mercury or copper clippings. A portion of the acid is decomposed, one-third of the oxygen of the sulphuric oxide being transferred to the metal, while the sulphuric oxide is reduced to sulphurous oxide which escapes as gas:

$$\underset{\text{Sulphuric acid.}}{2(H_2O.SO_3)} + Cu = \underset{\text{Copper sulphate.}}{CuO.SO_3} + 2H_2O + SO_2.$$

Another very simple method of preparing sulphurous oxide consists in heating concentrated sulphuric acid with sulphur; a very regular evolution of sulphurous oxide is thus obtained.

Sulphurous oxide is a colourless gas, having the peculiar suffocating odour of burning brimstone; it instantly extinguishes flame, and is quite irrespirable. Its density is 2·21; a litre weighs 2·8605 grams; 100 cubic inches weigh 68·69 grains. At 0° F. (−17·8° C.), under the ordinary pressure of the atmosphere, this gas condenses to a colourless, limpid liquid, very expansible by heat. Cold water dissolves more than thirty times its volume of sulphurous oxide. The solution, which contains hydrogen sulphite or sulphurous acid, may be kept unchanged so long as air is excluded, but access of oxygen gradually converts the sulphurous into sulphuric acid, although dry sulphurous oxide and oxygen gases may remain in contact for any length of time without change. When sulphurous oxide and aqueous vapour are passed into a vessel cooled to below 17° or 21° F. (−8·3° or −6° C.), a crystalline body forms, which contains about 24·2 sulphurous oxide to 75·8 of water.

One volume of sulphurous oxide gas contains one volume of oxygen and half a volume of sulphur vapour, condensed into one volume.

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* From πολύ, many, and θεῖον, sulphur.

Sulphurous oxide, like other gases which are freely soluble in water, must be collected by displacement, or by the use of the mercurial pneumatic trough. The manipulation with the latter is exactly the same in principle as with the ordinary water trough, but rather more troublesome, from the great density of the mercury, and its opacity. The whole apparatus is on a much smaller scale. The trough is best constructed of hard, sound wood, and so contrived as to economise as much as possible the expensive liquid it is to contain.

Sulphurous acid has bleaching properties; it is used in the arts for bleaching woollen goods and straw-plait. A piece of blue litmus-paper plunged into the moist gas is first reddened and then slowly bleached.

The sulphites of the alkalis are soluble and crystallisable; they are easily formed by direct combination. The sulphites of barium, strontium, and calcium are insoluble in water, but soluble in hydrochloric acid. The stronger acids decompose them; nitric acid converts them into sulphates. The soluble sulphites act as powerful reducing agents, and are much used in that capacity in chemical analysis.

Sulphurous oxide unites, under peculiar circumstances, with chlorine, and also with iodine, forming compounds which have been called chloro- and iodo-sulphuric acids. They are decomposed by water. It also combines with dry ammoniacal gas; and with nitric oxide in presence of an alkali.

Sulphur Trioxide, or **Sulphuric Oxide**, SO_3 (also called *Anhydrous Sulphuric acid*, or *Sulphuric anhydride*).—This compound may be formed directly by passing a dry mixture of sulphurous oxide and oxygen gases over heated spongy platinum; or it may be obtained by distilling the most concentrated sulphuric acid with phosphoric oxide, which then abstracts the water and sets the sulphuric oxide free. It is usually prepared, however, from the fuming oil of vitriol of Nordhausen, which may be regarded as a solution of sulphuric oxide in sulphuric acid. On gently heating this liquid in a retort connected with a receiver cooled by a freezing mixture, the sulphuric oxide distils over in great abundance, and condenses into beautiful white silky crystals, resembling those of asbestos.

Sulphuric oxide is also produced in considerable quantity by the following process. Vapour of ordinary strong sulphuric acid is passed through a white-hot platinum tube, whereby it is almost completely resolved into water, oxygen, and sulphurous oxide:

$$H_2SO_4 = H_2O + O + SO_2.$$

These mixed gases, after passing through a leaden worm to condense the greater portion of the water, are dehydrated by passing thme through a leaden tower filled with coke, over which a stream of concentrated sulphuric acid is allowed to trickle; and finally, the dry mixture of oxygen and sulphurous oxide is passed through platinum tubes heated to low redness and containing fragments of platinised pumice, whereupon they recombine to form sulphuric oxide, which is condensed in a series of Woulffe's bottles. This process bids fair to succeed as a manufacturing operation.*

Sulphuric oxide, when thrown into water, hisses like a red-hot iron, from the violence with which combination occurs: the product is sulphuric acid. When exposed to the air, even for a few moments, it liquefies by absorption of moisture. It unites with ammoniacal gas, forming a salt called ammonium sulphamate, the nature of which will be explained further on.

Sulphuric oxide is susceptible of two modifications (α and β), differing in their properties, though identical in composition. Bodies thus related are said to be isomeric (from ἴσος, equal, and μέρος, part). There are but few examples of this relation amongst inorganic compounds, but it is of frequent occurrence in organic chemistry. The α-modification, formed by cooling the liquid oxide, solidifies at +16° in long colourless prisms which melt at the same temperature; it boils at 46°; and its vapour at 20° has a tension represented by 200 millimeters of mercury. β—*Sulphuric oxide* is produced from the α-modification at temperatures below 25°; above 27° the transformation does not go on. It forms extremely fine white needles; at temperatures above 50° it gradually liquefies and passes into the first modification. Liquid sulphuric oxide undergoes very great expansion by heat, its mean coefficient of expansion between 25° and 45° being 0·0027 for 1° C., that is to say, more than two-thirds as great as that of gases. The two modifications differ greatly in their relations to solvents. Liquid sulphuric oxide mixes in all proportions with hydrogen sulphate, H_2SO_4; the β-oxide dissolves in sulphuric acid with extreme slowness, and gradually separates from a mixture of 10 parts SO_3 and 1–2 parts H_2SO_4. With a larger proportion of the acid, no solid oxide separates, even on cooling to a low temperature; if the proportion of acid, H_2SO_4, amounts to 5 parts for 10 parts of oxide, the mixture may deposit crystals of pyrosulphuric acid, $H_2S_2O_7$ or $H_2SO_4.SO_3$.

Sulphuric Acid, H_2SO_4.—The preparation of this important acid depends upon the fact that, when sulphurous oxide, nitrogen tetroxide, and water are present together in certain proportions, the sulphurous oxide becomes oxidised at the expense of the nitrogen tetroxide, which, by the loss of one-half of its oxygen, sinks to the condition of nitrogen dioxide. The operation is thus conducted:

A large and very long chamber is built of sheet-lead supported by timber framing; on the outside, at one extremity, a small furnace or oven is constructed, having a wide tube leading into the chamber. In this, sulphur is kept burning, the flame of which heats a crucible containing a mixture of nitre and oil of vitriol.

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* Messel and Squire, Chemical News, 1876, i. 177.

A shallow stratum of water occupies the floor of the chamber, and a jet of steam is also introduced. Lastly, an exit is provided at the remote end of the chamber for the spent and useless gases. The effect of these arrangements is to cause a constant supply of sulphurous oxide, atmospheric air, nitric acid vapour, and water in the state of steam, to be thrown into the chamber, there to mix and react upon each other. The nitric acid immediately gives up a part of its oxygen to the sulphurous oxide, and is itself reduced to nitrogen tetroxide, N_2O_4 or NO_2; it does not remain in this state, however, but suffers further deoxidation until it becomes reduced to nitrogen dioxide, N_2O_2 or NO. That substance, in contact with free oxygen, absorbs a portion of the latter, and once more becomes tetroxide, which is again destined to undergo deoxidation by a fresh quantity of sulphurous oxide. A very small portion of nitrogen tetroxide, mixed with atmospheric air and sulphurous oxide, may thus in time convert an indefinite amount of the latter into sulphuric acid, by acting as a kind of carrier between the oxygen of the air and the sulphurous oxide. The presence of water is essential to this reaction, which may be represented by the equation,

$$NO_2 + SO_2 + H_2O = NO + H_2SO_4.$$

Such is the simplest view that can be taken of the production of sulphuric acid in the leaden chamber; but it is too much to affirm that it is strictly true; the reaction may be more complex. When a little water is put at the bottom of a large glass globe, so as to maintain a certain degree of humidity in the air within, and sulphurous oxide and nitrogen tetroxide are introduced by separate tubes, symptoms of chemical action become immediately evident, and after a little time a white crystalline matter is observed to condense on the sides of the vessel. This substance appears to be a compound of sulphuric acid, nitrous acid, and a little water.* When thrown into water, it is resolved into sulphuric acid, nitrogen dioxide, and nitric acid. This curious body is certainly very often produced in large quantity in the leaden chambers; but that its production is indispensable to the success of the process, and constant when the operation goes on well and the nitrogen tetroxide is not in excess, may perhaps admit of doubt.

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* Gaultier de Claubry assigned to this substance the composition expressed by the formula $2(N_2O_3.2H_2O_3).5SO_3$, and this view has generally been received by recent chemical writers. De la Provostaye has since shown that a compound possessing all the essential properties of the body in question may be formed by bringing together, in a sealed glass tube, liquid sulphurous oxide and liquid nitrogen tetroxide, both free from water. The white crystalline solid soon begins to form, and at the expiration of twenty-six hours the reaction appears complete. The new product is accompanied by an exceedingly volatile greenish liquid having the characters of nitrous acid. The white substance, on analysis, was found to contain the elements of two molecules of sulphuric oxide, and one of nitrous oxide, or $N_2O_3.2SO_3$. De la Provostaye explains the anomalies in the different analyses of the leaden-chamber product, by showing that the pure substance forms crystallisable combinations with different proportions of sulphuric acid. (Ann. Chim. Phys. lxxiii. 362.) See also Weber (Jahresbericht für Chemie, 1863, p. 738; 1865, p. 93; Bull. Soc. Chim. de Paris, 1867, i. 15).

The water at the bottom of the chamber thus becomes loaded with sulphuric acid: when a certain degree of strength has been reached, the acid is drawn off and concentrated by evaporation, first in leaden pans, and afterwards in stills of platinum, until it attains a density (when cold) of 1·84, or thereabouts; it is then transferred to carboys, or large glass bottles fitted in baskets, for sale. In Great Britain this manufacture is one of great national importance, and is carried on to a vast extent.

Sulphuric acid is now more frequently made by burning iron pyrites, or poor copper ore, or zinc-blende, instead of Sicilian sulphur: as thus prepared it very frequently contains arsenic, from which it may be freed, however, by heating it with a small quantity of sodium chloride, or by passing through the heated acid a current of hydrochloric acid gas, whereby the arsenic is volatilised as trichloride.

The most concentrated sulphuric acid, or *oil of vitriol*, as it is often called, is a definite combination of 40 parts sulphuric oxide and 9 parts of water, and is represented by the formula, $H_2O.SO_3$ or H_2SO_4. It is a colourless oily liquid, having a specific gravity of about 1·85, of intensely acid taste and reaction. Organic matter is rapidly charred and destroyed by it At the temperature of $-26°$ C. ($-15°$ F.) it freezes; at 327° C. (620° F.) it boils, and may be distilled without decomposition. Oil of vitriol has a most energetic attraction for water; it withdraws aqueous vapour from the air, and when it is diluted with water, great heat is evolved, so that the mixture always requires to be made with caution. Oil of vitriol is not the only hydrate of sulphuric oxide; three others are known to exist. When the fuming oil of vitriol of Nordhausen is exposed to a low temperature, a white crystalline substance separates, which is a hydrate containing half as much water as the common liquid acid. Further, a mixture of 98 parts of strong liquid acid and 18 parts of water, $2H_2O.SO_3$ or $H_2SO_4.H_2O$, congeals or crystallises at a temperature above 0° C., and remains solid even at 7·2° C. (45° F.) Lastly, when a very dilute acid is concentrated by evaporation in a vacuum over a surface of oil of vitriol, the evaporation stops when the sulphuric oxide and water bear to each other the proportion of 80 to 54, answering to the formula, $3H_2O.SO_3$ or $H_2SO_4.2H_2O$.

When the vapour of sulphuric acid is passed over red-hot platinum, it is decomposed into oxygen and sulphurous acid. St. Claire Deville and Debray have recommended this process for the preparation of oxygen on the large scale, the sulphurous acid being easily separated by its solubility in water or alkaline solutions.

Sulphuric acid acts readily on metallic oxides; converting them into sulphates. It also decomposes carbonates with the greatest ease, expelling carbon dioxide with effervescence. With the aid of heat it likewise decomposes all other salts containing acids more volatile than itself. The sulphates are a very important class of salts, many of them being extensively used in the arts. Most sulphates are soluble in water, but they are all insoluble in alcohol. The barium, calcium, strontium, and lead salts are insoluble, or very slightly soluble, in water: and are formed by precipitating a soluble salt of either of those metals with sulphuric acid, or a soluble metallic sulphate. Barium sulphate is quite insoluble in water: consequently sulphuric acid, or its soluble salts, may be detected with the greatest ease by solution of barium nitrate or chloride: a white precipitate is thereby formed which does not dissolve in nitric or hydrochloric acid.

Disulphuric or **Pyrosulphuric Acid,** $H_2S_2O_7$ (also called *Fuming Sulphuric Acid* and *Nordhausen Sulphuric Acid.*)—This acid contains the elements of one molecule of sulphuric oxide, and one molecule of sulphuric acid, or of two molecules of sulphuric acid *minus* one molecule of water:

$$H_2S_2O_7 = SO_3.H_2SO_4 = 2H_2SO_4 - H_2O.$$

It may be obtained of definite composition and in the crystalline form by adding liquid sulphuric oxide to strong sulphuric acid, in the proportions above indicated. The resulting crystals melt at 35°. This acid was originally prepared at Nordhausen in Saxony from an impure ferric sulphate obtained by exposing ordinary ferrous sulphate (green vitriol) to a moderate heat in contact with the air. This ferric sulphate is distilled in sulphur retorts arranged in a reverberatory furnace, and the distillate, consisting chiefly of sulphuric oxide, is received in a small quantity of water, or more frequently in ordinary strong sulphuric acid. A brown fuming liquid is thus obtained which agrees nearly in composition with the formula $H_2S_2O_7$, has a specific gravity of 1·9, solidifies at 0° to colourless crystals, and is resolved at a gentle heat into SO_3 which distils over, and H_2SO_4 which remains behind.

The manufacture of fuming sulphuric acid in the manner just described was first practised at Nordhausen in Saxony, and appears to have been known since the fifteenth century: but it is now carried on almost exclusively in Bohemia. An easier and more productive method of obtaining the sulphuric oxide required for its formation is that of Messel and Squire, already described (p. 209.) Fuming sulphuric acid was until lately employed only for dissolving indigo, but it is now used in very large quantities for dissolving anthraquinone for the manufacture of artificial alizarin. (See Organic Chemistry).

The pyrosulphates, that of potassium, for example, which has the composition $K_2S_2O_7$, or $K_2SO_4.SO_3$, are prepared by the action of sulphuric oxide on the corresponding sulphates. When strongly heated, they give off sulphuric oxide, and are converted into sulphates.

Hyposulphurous Acid, H_2SO_2 (also called *Hydrosulphurous Acid*).—This acid is formed by the action of zinc on an aqueous solution of sulphurous acid. The zinc dissolves without evolution of hydrogen, merely removing an atom of oxygen. A yellow solution is thereby formed which possesses much greater decolorising power than sulphurous acid itself, and quickly reduces the metals from salts of silver and mercury. This solution is, however, very unstable, and quickly loses its bleaching power. A more definite product is obtained by immersing clippings of zinc in a concentrated solution of acid sodium sulphite $NaHSO_3$, contained in a closed vessel, whereby sodium hyposulphite, Na_2SO_2, and zinc-sodium sulphite, $Na_2Zn(SO_3)_2$, are produced, the latter crystallising out. To isolate the hyposulphite, the liquid is decanted, after about half an hour, into a flask three-fourths filled with strong alcohol, and the flask is sealed. A crystalline precipitate immediately forms, consisting for the most part of zinc-sodium sulphite, while nearly all the hyposulphite remains dissolved in the alcohol. The solution, decanted into a flask quite filled with it, well closed, and left in a cool place, solidifies in a few hours to a mass of slender colourless needles, consisting of sodium hyposulphite, which must be quickly pressed between folds of linen, and dried in a vacuum, as it becomes very hot if exposed to the air in the moist state; when dry, however, it is not affected by oxygen. This salt is very soluble in water, soluble also in dilute alcohol, the solutions exhibiting all the bleaching and reducing properties above described. The crystals when exposed to the air are completely converted into acid sodium sulphite, $Na\,HSO_3$. By heating them with oxalic acid, hyposulphurous acid is obtained, as a deep orange-coloured strongly bleaching liquid, which quickly decomposes, becoming colourless, and depositing sulphur.*

Thiosulphuric Acid, $H_2S_2O_3$ (formerly called *Hyposulphurous Acid*).—By digesting sulphur with a solution of potassium or sodium sulphite, a portion of that substance is dissolved, and the liquid, by slow evaporation, furnishes crystals of thiosulphate: $Na_2SO_3 + S = Na_2S_2O_3$. The acid itself is scarcely known, for it cannot be isolated; when hydrochloric acid is added to a solution of a thiosulphate, the acid of the latter is almost instantly resolved into sulphur, which precipitates, and sulphurous acid, easily recognised by its odour. In a very dilute solution, however, it appears to remain undecomposed for some time. The alkaline thiosulphates readily dissolve certain salts of silver, as the chloride, which are insoluble in water—a property which has conferred upon them a considerable share of importance in relation to the art of photography. They are also much used as antichlores for removing the last traces of chlorine from bleached goods.

Seleniosulphuric Acid, H_2SeSO_3.—This acid, having the composition of sulphuric acid in which 1 atom of oxygen is replaced by selenium, is formed by direct addition of selenium to sulphurous acid. When selenium is digested with a solution of neutral potassium sulphite, and the easily decomposible liquid, after being filtered from the selenium which separates on cooling and dilution with water, is left to evaporate at ordinary temperatures, there crystallises out, first a sparingly soluble seleniferous salt in small shining prisms, afterwards a much more soluble salt, which is the chief product of the reaction, while the excess of sulphite remains in the mother-liquor.

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* Schützenberger, Zeitchrift für Chemie, 1869, p. 545.

The more soluble seleniferous salt is potassium seleniosulphate, K_2SeSO_3. It is likewise formed, together with thiosulphate, when a solution of potassium selenide is mixed with sulphurous acid. It crystallises readily, even from small quantities of solution, in large, very thin, six-sided tables belonging to the rhombic system, which deliquesce in moist air, and effloresce with partial loss of water over oil of vitriol. When heated they turn brown and yield a polysulphide of potassium. Water separates selenium from them, and the filtered solution yields by evaporation crystals which again react in the same way with water, so that, by repeated crystallisation, the whole of the seleniosulphate may be decomposed; the liquid then contains seleniotrithionate. Acids, even sulphurous acid, throw down the whole of the selenium from the aqueous solution; barium chloride and baryta-water precipitate barium sulphite and selenium; calcium and manganese salts give rise to a similar decomposition. With ammoniacal silver solution the seleniosulphate forms a precipitate of silver selenide, together with potassium sulphate:

$$K_2SeSO_3 + Ag_2O = Ag_2Se + K_2SO_4.$$

The sulphites of sodium, ammonium, and magnesium react with selenium in the same manner as the potassium salt, the magnesium salt, however, very slowly. The seleniosulphates of sodium and ammonium are very unstable.

Dithionic or **Hyposulphuric Acid,** $H_2S_2O_6$.—This acid is prepared by suspending finely divided manganese dioxide in water artificially cooled, and then transmitting a stream of sulphurous acid gas; the dioxide becomes monoxide, half its oxygen converting the sulphurous into dithionic acid: $MnO_2 + 2SO_2 = MnS_2O_6$. The manganese dithionate thus prepared is decomposed by a solution of pure barium hydrate, and the barium salt, in turn, by enough sulphuric acid to precipitate the base. The solution of dithionic acid may be concentrated by evaporation in a vacuum, until it acquires a density of 1·347; on further concentration, it decomposes into sulphuric and sulphurous acids. It has no odour, is very sour, and forms soluble salts with baryta, lime, and lead oxide.

Trithionic Acid, $H_2S_3O_6$.—A substance accidentally formed by Langlois, in the preparation of potassium thiosulphate, by gently heating with sulphur a solution of potassium carbonate saturated with sulphurous acid. It is also produced by the action of sulphurous oxide on potassium thiosulphate: $2K_2S_2O_3 + 3SO_2 = 2K_2S_3O_6 + S$. Its salts bear a great resemblance to those of thiosulphuric acid, but differ completely in composition, while the acid itself is not quite so prone to change. It is obtained by decomposing the potassium salt with hydrofluosilicic acid: it may be concentrated under the receiver of the air-pump, but is gradually decomposed into sulphur, sulphurous and sulphuric acids.

Tetrathionic Acid, $H_2S_4O_6$.—This acid was discovered by Fordos and Gelis. When iodine is added to a solution of barium thiosulphate, a large quantity of that substance is dissolved, and a clear colourless solution obtained, which, besides barium iodide, contains barium tetrathionate: $2BaS_2O_3 + I_2 = BaI_2 + BaS_4O_6$. By suitable means, the acid can be eliminated, and obtained in a state of solution. It very closely resembles dithionic acid. The same acid is produced by the action of sulphurous acid on chlorine disulphide.

Pentathionic Acid, $H_2S_5O_6$.—This acid was discovered by Wackenroder, who formed it by the action of hydrogen sulphide on sulphurous acid: $5H_2SO_3 + 5H_2S = H_2S_5O_6 + 9H_2O + S_5$. It is colourless and inodorous, of acid and bitter taste, and capable of being concentrated to a considerable extent by cautious evaporation.

Under the influence of heat, it is decomposed into sulphur, sulphurous, and sulphuric acids, and hydrogen sulphide. The salts of pentathionic acid are nearly all soluble. The barium salt crystallises from alcohol in square prisms. The acid is also formed when lead dithionate is decomposed by hydrogen sulphide, and when chlorine monosulphide is heated with sulphurous acid.

Sulphur with Hydrogen.

Hydrogen Monosulphide—*Sulphydric Acid; Hydrosulphuric Acid; Sulphuretted Hydrogen,* H_2S.—There are two methods by which this important compound can be readily prepared, namely, by the action of dilute sulphuric acid upon iron monosulphide, and by the decomposition of antimony trisulphide with hydrochloric acid. The first method yields it most easily, the second in the purest state.

Iron monosulphide is put into the apparatus for hydrogen, already several times mentioned, together with water, and oil of vitriol is added by the funnel, until a copious disengagement of gas takes place. This is to be collected over tepid water. The reaction is thus explained:—

FeS	+	H_2SO_4	=	H_2S	=	$FeSO_4$
Ferrous sulphide.		Hydrogen sulphate.		Hydrogen sulphide.		Ferrous sulphate.

By the other plan, finely powdered antimony trisulphide is put into a flask to which a cork and bent tube can be adapted, and strong liquid hydrochloric acid poured upon it. On the application of heat, a double interchange occurs, hydrogen sulphide and antimony trichloride being formed. The action lasts only while the heat is maintained.

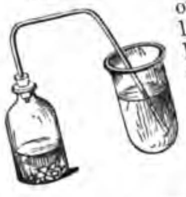
$$\underset{\text{Antimonious sulphide.}}{Sb_2S_3} + \underset{\text{Hydrogen chloride.}}{6HCl} = \underset{\text{Hydrogen sulphide.}}{3SH_2} + \underset{\text{Antimonious chloride.}}{2SbCl_3}$$

Hydrogen sulphide is a colourless gas, having the odour of putrid eggs; it is most offensive when in small quantity, when a mere trace is present in the air. It is not irritant, but, on the contrary, powerfully narcotic. When set on fire, it burns with a blue flame, producing sulphurous acid when the supply of air is abundant, and depositing sulphur when the oxygen is deficient. Mixed with chlorine, it is instantly decomposed, with separation of the whole of the sulphur.

This gas has a specific gravity of 1·171 referred to air, or 17 referred to hydrogen as unity; a liter weighs 1·51991 grams.

A pressure of 17 atmospheres at 10° reduces it to the liquid form. Cold water dissolves its own volume of hydrogen sulphide, and the solution is used as a test; it is, however, somewhat prone to decomposition by the oxygen of the air, and should therefore be kept in a tightly closed bottle. Another mode of testing with hydrogen sulphide is to keep a little apparatus for generating the gas always at hand. A small bottle or flask, to which a bit of bent tube is fitted by a cork, is supplied with a little iron sulphide and water; when it is required for use, a few drops of oil of vitriol are added, and the gas is at once evolved. The experiment completed, the liquid is poured from the bottle, replaced by a little clean water, and the apparatus is again ready for use.

Fig. 122.



Potassium heated in hydrogen sulphide burns with great energy, becoming converted into sulphide, while pure hydrogen remains, equal in volume to the original gas. Taking this fact into account, and comparing the density of the gas with those of hydrogen and sulphur vapour, i appears that every volume of hydrogen sulphide contains or volume of hydrogen and half of a volume of sulphur-vapour, th whole condensed into one volume, a constitution precisely analogo to that of water-vapour. This corresponds with its composition weight, determined by other means—namely, 16 parts sulphur one part hydrogen.

When a mixture of 100 measures of hydrogen sulphide and measures of pure oxygen is exploded by the electric spark, com combustion ensues, and 100 measures of sulphurous oxide gas are produced.

Hydrogen sulphide is a frequent product of the putrefaction of organic matter, both animal and vegetable; it occurs also in certain mineral springs, as at Harrogate and elsewhere. When accidentally present in the atmosphere of an apartment, it may be instantaneously destroyed by a small quantity of chlorine gas.

There are few re-agents of greater value to the practical chemist than this substance: when brought in contact with many metallic solutions, it gives rise to precipitates, which are often exceedingly characteristic in appearance, and it frequently affords the means of separating metals from each other with the greatest precision and certainty. These precipitates are insoluble sulphides, formed by the mutual decomposition of the metallic oxides or chlorides and hydrogen sulphide, water or hydrochloric acid being produced at the same time. All the metals are, in fact, precipitated, whose sulphides are insoluble in water and in dilute acids.

Arsenic and cadmium solutions thus treated give bright yellow precipitates, the former soluble, the latter insoluble, in ammonium sulphide: tin-salts give a brown or a yellow precipitate, according as the metal is in the form of a stannous or a stannic salt; both soluble in ammonium sulphide. Antimony solutions give an orange-red precipitate, soluble in ammonium sulphide. Copper, lead, bismuth, mercury, and silver salts give dark-brown or black precipitates, insoluble in ammonium sulphide; gold and platinum salts, black precipitates, soluble in ammonium sulphide.

Hydrogen sulphide possesses the properties of an acid: its solution in water reddens litmus-paper.

The best test for the presence of this compound is paper wetted with solution of lead acetate. This salt is blackened by the smallest trace of the gas.

Hydrogen Persulphide.—This very unstable substance is prepared by the following means:—

Equal weights of slaked lime and flowers of sulphur are boiled with 5 or 6 parts of water for half an hour, whereby a deep orange-coloured solution is produced, containing among other things, calcium disulphide. This is filtered, and slowly added to an excess of dilute sulphuric acid, with constant agitation. A white precipitate of separated sulphur and calcium sulphate then makes its appearance, together with a quantity of yellow oily-looking matter, which collects at the bottom of the vessel: this is hydrogen persulphide.

This compound is generally regarded as a disulphide of hydrogen, H_2S_2, analogous to the dioxide, but its great instability prevents the determination of its composition by direct analysis. Hofmann, however, by treating strychnine in alcoholic solution with ammonium sulphide containing free sulphur, has obtained an orange-red crystalline compound, $C_{21}H_{22}N_2O_2.H_2S_3$, which is resolved by sulphuric acid into soluble strychnine sulphate and a yellow oily liquid resembling the persulphide of hydrogen obtained as above. Hence it might be inferred that this persulphide is really a sesquisulphide H_2S_3; but it begins to decompose as soon as separated.* On the other hand, E. Schmidt, by treating an alcoholic solution of strychnine with sulphuretted hydrogen, has obtained a compound containing $2C_{21}H_{22}N_2O_2.3H_2S_2$. The composition of hydrogen persulphide must therefore be regarded as still undecided.

Hydrogen persulphide dissolves phosphorus and iodine, forming a phosphorus sulphide and hydrogen iodide respectively, with evolution of sulphuretted hydrogen. With chlorine it forms hydrochloric acid and sulphur chloride, S_2Cl_2. Bromine acts in a similar manner. Ammonia, either gaseous or in aqueous solution, decomposes it instantly, leaving sulphur in a peculiarly brittle, blistered state. It is remarkable that sulphurous acid, which rapidly decomposes hydrogen monosulphide, with separation of sulphur, has scarcely any action on the persulphide.†

Carbon and Sulphur.

Two compounds of these elements are known, viz.; the disulphide, produced by the direct combination of its elements at a high temperature, and the monosulphide, produced by reduction of the disulphide.

Carbon Disulphide, or **Bisulphide,** CS_2.—To prepare this compound a wide porcelain tube filled with pieces of charcoal which have been recently heated to redness in a covered crucible, is fixed across a furnace in a slightly inclined position. Into the lower extremity a tolerably wide tube is secured by the aid of a cork: this tube bends downwards, and passes nearly to the bottom of a bottle filled with fragments of ice and a little water. The porcelain tube being heated to bright redness, fragments of sulphur are thrown into the open end, which is immediately afterwards stopped by a cork. The sulphur melts, and becomes converted into vapour, which at that high temperature combines with the carbon, forming an exceedingly volatile compound, which is condensed by the ice and collects at the bottom of the vessel. This is collected and redistilled at a very gentle heat in a retort connected with a good condenser.

For preparation on the large scale, a tubulated earthen retort is filled with charcoal, and the sulphur is dropped in through a porcelain tube passing through the tubulus and reaching nearly to the bottom; or the charcoal is contained in a large iron cylinder, and the sulphur introduced through a pipe fitted into the lower part.

Carbon disulphide is a transparent, colourless liquid of great refractive and dispersive power. Its density is 1·272, that of its vapour is 2·67. It boils at 43°, and emits vapour of considerable elasticity at common temperatures. In its ordinary state, it has a very repulsive odour, due perhaps to the presence of small quantities of other volatile sulphur-compounds; but when these are removed by agitating the liquid with mercury till it ceases to blacken the bright surface of the metal, it is said to have a pure ethereal odour. When set on fire in the air, it burns with a blue flame, forming carbon dioxide and sulphur dioxide; and when its vapour is mixed with oxygen, it becomes explosive. Carbon disulphide, when heated with water in a sealed tube to about 153°, is converted into carbon dioxide and hydrogen sulphide. In contact with nascent hydrogen (when heated with zinc and dilute sulphuric acid), it is converted into a white crystalline substance, having the composition CH_2S, crystallising in square prisms, insoluble in water, alcohol, and ether, but soluble in carbon disulphide, subliming at 150°, and decomposing at 200°. Carbon disulphide freely disolves sulphur, and by spontaneous evaporation deposits the latter in beautiful crystals; it also dissolves phosphorus, iodine, camphor, and caoutchouc, and mixes easily with oils. It is extensively used in the vulcanisation of caoutchouc, and in the manufacture of gutta percha; also for extracting bitumen from mineral substances, and oil from seeds.

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* Berichte der deutsch Chem. Gesellschaft, 1868, p. 81.

† Liebig's Annalen, clxxx. 287.

‡ W. Ramsay, Chem. Soc. Journ. 1874, 857.

Carbon disulphide unites with metallic sulphides, forming salts called sulphocarbonates, which have the composition of carbonates with the oxygen replaced by sulphur.

Calcium carbonate, $CaCO_3 = CaO.CO_2$
Calcium sulphocarbonate, $CaCS_3 = CaS.CS_2$
Hydrogen sulphocarbonate, $H_2CS_3 = H_2S.CS_2$

By treating the ammonium salt with dilute sulphuric or hydrochloric acid, an oily acid liquid is precipitated, consisting of hydroden sulphocarbonate, or sulphocarbonic acid.

Carbon Monosulphide, CS, recently discovered by Sidot,* is obtained by exposing the disulphide in sealed tubes for a considerable time to direct sunshine. It is then precipitated as a brown powder, which may be purified by distilling off the undecomposed disulphide, and washing the residual mixture of monosulphide and free sulphur with pure disulphide till all the free sulphur is removed. It is a maroon-coloured powder, without taste or smell, and having a specific gravity of 1·66. It is insoluble in water, alcohol, turpentine-oil, and benzene, slightly soluble at the boiling heat in carbon disulphide and in ether. It disolves also in caustic potash and in boiling nitric acid; the strongest nitric acid ignites it. At about 200° it is resolved into its elements, a small quantity of the disulphide being formed at the same time.

According to S. Kern,† carbon monosulphide is also formed by the prolonged action of iron wire on the disulphide in sealed tubes.

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* Comptes Rendus, lxxxi. 32.

† Chemical News, xxxiii. 253.

Carbon Oxysulphide, COS.—This compound, discovered by Than, is produced by direct combination when carbon monoxide mixed with sulphur-vapour is passed through a red-hot porcelain tube. As thus prepared it is mixed with free carbon monoxide; but on passing the gas through alcoholic potash, the oxysulphide is alone absorbed, and may be liberated in the pure state by treating the solution with hydrochloric acid.

Carbon oxysulphide is also produced by gently heating the disulphide with an equivalent quantity of sulphur trioxide: $CS_2 + SO_3 = CSO + SO_2 + S$; and by decomposing potassium sulphocyanate with moderately dilute-acids: sulphocyanic acid HCNS is then liberated and decomposed by the water present in the manner represented by the equation—

$$HCSN + H_2O = NH_3 + CSO.$$

Carbon oxysulphide is a gas of sp. gr. 2·1046, and may easily be poured from one vessel to another. It has an aromatic odour like that of some resins, slightly also that of hydrogen sulphide, and a feebler acid reaction than carbon dioxide. At a low red heat it is partly resolved into carbon monoxide and sulphur-vapour; by a fine platinum wire ignited by the electric current, it is slowly but completely decomposed, yielding an equal volume of carbon monoxide. It burns in the air with a faint blue flame, producing carbon dioxide and sulphur dioxide; with 1½ vol. oxygen, it forms an explosive mixture burning with a shining bluish-white flame. It is not acted upon by chlorine or fuming nitric acid at ordinary temperatures, and does not form an explosive mixture with nitrogen dioxide.

Water absorbs about its own volume of carbon oxysulphide, acquiring a sweetish and afterwards a pungent taste, and decomposing it after some time. It appears to exist in some sulphur springs and in the sulphurous gases of volcanos. Potash-solution absorbs the gas as completely as carbon dioxide, though less quickly; the solution exhibits the reactions of metallic sulphides, and when treated with acids gives off hydrogen sulphide and carbon dioxide. Baryta water, and lime-water act in a similar manner. Neutral or acid solutions of lead, copper, cadmium, and silver salts are not precipitated by the gas, but when mixed with excess of ammonia they yield with it characteristic precipitates of metallic sulphides. *

Sulphur and Chlorine.

Three chlorides of sulphur are known, represented by the formulæ, S_2Cl_2, SCl_2, and SCl_4.

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* See further, Watts's Dictionary of Chemistry, First Supplement, p. 406; *Second* Supplement, p. 262.

The *monochloride*, SCl or S_2Cl_2, which may also be regarded as a disulphide of chlorine, analogous in composition to hydrogen dioxide, is prepared by passing dry chlorine-gas into a retort in which sulphur is sublimed at a gentle heat. It then distils over, and may be collected in a receiver surrounded by cold water, and freed from excess of sulphur by rectification. It is also produced by distilling a mixture of 1 part sulphur with 9 parts stannic chloride, or 8·5 parts mercuric chloride.

Disulphide of chlorine is a mobile reddish-yellow liquid, having a peculiar, penetrating, disagreeable odour, and fuming strongly in the air. Specific gravity = 1·687. It boils at 136°. It dissolves in carbon disulphide, alcohol, and ether, not however without decomposition in the two latter. It dissolves sulphur in large quantities, especially when heated. When saturated with sulphur at ordinary temperatures, it forms a clear yellow liquid of specific gravity 1·7, and containing altogether 66·7 per cent. sulphur. The solution of chlorine disulphide with excess of sulphur in crude benzol, is used for vulcanising or sulphurising caoutchouc. It is instantly decomposed by water, with formation of hydrochloric and thiosulphuric acids, and separation of sulphur, the thiosulphuric acid in its turn decomposing into sulphur and sulphurous acid, $2S_2Cl_2 + 3H_2O = 4HCl + S_2 + H_2S_2O_3$ (or $H_2SO_3 + S$).

The *dichloride*, SCl_2, is produced by passing chlorine to saturation into the preceding compound cooled by a mixture of ice and salt, and expelling the excess of chlorine by a stream of carbon dioxide. The product is a deep-red liquid boiling at 164°, and containing 30·5 per cent. of sulphur, 69·5 of chlorine, agreeing nearly with the formula SCl_2, which requires 31·07 per cent. sulphur and 68·93 chlorine.

The *tetrachloride*, SCl_4, is prepared by saturating chlorine disulphide with chlorine at $-20°$. The product contains 81·59 per cent. chlorine and 18·41 sulphur, the numbers calculated from the formula SCl_4 being 81·61 and 18·39. Sulphur tetrachloride is acted upon by sulphuric oxide, producing sulphurous chloride together with chlorine and sulphurous oxide: thus,

$SCl_4 + SO_3 = SOCl_2 + Cl_2 + SO_2$[*]

Oxychlorides. — 1. *Sulphurous Chloride*, $SOCl_2$. — This compound, also called *Chloride of Thionyl*, is derived from sulphurous acid, SO_3H_2 or SO.HO.HO, by the substitution of 2Cl for 2HO. It is formed by the action of water, alcohols, acids, &c. on the sulphides of chlorine; but is more easily prepared by the action of phosphorus pentachloride on sulphurous oxide, or by that of phosphorus oxychloride on sulphite of calcium :

$$SO_2 + PCl_5 = POCl_3 + SOCl_2.$$
$$3CaSO_3 + 2POCl_3 = Ca_3P_2O_8 + 3SOCl_2.$$

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[*] Respecting other reactions of the chlorides of sulphur, and especially their decomposition by heat, see Watts's Dictionary of Chemistry, Second Supplement, p. 1129.

It is separated by distillation from the fixed calcium phosphate produced simultaneously in the second, and by fractional distillation from the phosphorus oxychloride produced in the first reaction.

Sulphurous chloride is a colourless, strongly refracting liquid, which boils at 82°. It is decomposed by water, yielding hydrochloric and sulphurous acids; and by alcohols with formation of alcoholic chlorides and sulphurous acid, thus :

$$SOCl_2 + 2H_2O = 2HCl + H_2SO_3$$
$$SOCl_2 + \underset{\text{Ethyl alcohol}}{2(C_2H_5)HO} = \underset{\text{Ethyl chloride.}}{2C_2H_5Cl} + H_2SO_3 .$$

Sulphuric chloride, or *Sulphuryl chloride*, SO_2Cl_2 (also called *Chlorosulphuric acid*) is formed by prolonged exposure of a mixture of chlorine and sulphurous oxide gases to strong sunshine; also, together with phosphorus oxychloride, by the action of phosphorus pentachloride on sulphuric oxide :

$$SO_3 + PCl_5 = POCl_3 + SO_2Cl_2 ;$$

but it is best prepared by distilling strong sulphuric acid with the pentachloride, or lead sulphate with the oxychloride of phosphorus :

$$H_2SO_4 + 2PCl_5 = SO_2Cl_2 + 2POCl_3 + 2HCl$$
$$3PbSO_4 + 2POCl_3 = 3SO_2Cl_2 + \underset{\text{Lead phosphate.}}{Pb_3P_2O_8}$$

Sulphuric chloride is a colourless fuming liquid, of specific gravity 1·66. It boils at 77°, and may be distilled unchanged over caustic lime or baryta. When poured into water, it sinks in the form of oily drops, which gradually disappear, being converted into hydrochloric and sulphuric acids:

$$SO_2Cl_2 + 2H_2O = 2HCl + H_2SO_4 .$$

With alcohol it behaves in a similar manner, thus :

$$SO_2Cl_2 + 2(C_2H_5)HO = 2C_2H_5Cl + H_2SO_4 .$$

In the actual reaction, however, the sulphuric acid is converted into ethylsulphuric acid by the intervention of another atom of alcohol.

$$H_2SO_4 + (C_2H_5)HO = H_2O + (C_2H_5)HSO_4 .$$

Sulphuric Hydroxychloride or **Chlorhydrate**, $HClSO_3$ or $SO_2.HO.Cl$ (also called *Chlorhydrosulphurous Acid.*)—This compound, discovered by Williamson, is intermediate in composition between *sulphuric* acid and sulphuric chloride, is derived from sulphuric acid SO_4H_2 or $SO_2.HO.HO$, by the substitution of 1Cl for 1HO. It is the first product of the action of phosphorus pentachloride on strong sulphuric acid:

$$SO_2.HO.HO + PCl_5 = POCl_3 + HCl + SO_2.HO.Cl.$$

As thus prepared it is mixed with sulphuric chloride; but it may be obtained pure by treating sulphuric acid with phosphorus oxychloride, hydrochloric acid and metaphosphoric acid being produced at the same time:

$$2(SO_2.HO.HO) + POCl_3 = 2(SO_2.HO.Cl) + HCl + HPO_3.$$

It is also formed by the action of water on sulphuric chloride:

$$SO_2Cl_2 + H_2O = HCl + HClSO_3.$$

Sulphuric hydroxychloride is a colourless liquid, which boils at about 150°, being at the same time partially resolved into sulphuric acid and sulphuric chloride: $2HClSO_3 = H_2SO_4 + Cl_2SO_2$. When poured into water, it sinks to the bottom and gradually dissolves, with formation of hydrochloric and sulphuric acids. It has decided acid properties, and forms definite salts in which its hydrogen is replaced by metals. Thus it dissolves sodium chloride at a gentle heat, with evolution of hydrochloric acid, and formation of the salt $NaClSO_3$.

Pyrosulphuric Chloride, $S_2O_5Cl_2$ or $(SO_2Cl)_2O$.—This compound is formed on heating together phosphorus pentachloride and sulphuric oxide:

$$PCl_5 + 2SO_3 = S_2O_5Cl_2 + POCl_3,$$

and by the action of phosphorus pentachloride on sulphuric hydroxychloride:

$$PCl_5 + 2SO_2ClOH = (SO_2Cl)_2O + POCl_3 + 2HCl.$$

It is a colourless oily liquid of sp. gr. 1·819 at 18°, boiling at 146°. In contact with water it decomposes slowly and noiselessly, and is thus distinguished from sulphuric hydroxychloride, which is rapidly decomposed, with almost explosive violence, when thrown into water. When heated above its boiling point, it is resolved into chlorine, sulphurous oxide and sulphuric oxide:

$$S_2O_5Cl_2 = SO_3 + SO_2 + Cl_2.$$

When submitted to the action of phosphorus pentachloride, it yields chlorine, sulphurous oxide, and phosphorus oxychloride:

$$S_2O_5Cl_2 + PCl_5 = POCl_3 + 2SO_2 + 2Cl_2.$$

Carbon Sulphochloride, $CSCl_2$.—This compound, the sulphur-analogue of carbonyl chloride or phosgene (p. 171), is produced, together with chlorine monosulphide, by the action of dry chlorine on carbon disulphide: $CS_2 + Cl_4 = SCl_2 + CSCl_2$, or by passing a mixture of hydrogen sulphide and vapour of carbon tetrachloride through a red-hot tube: $CCl_4 + H_2S = 2HCl + CSCl_2$. It is a yellow liquid having a very irritating odour, not acted upon by water or acids, but decomposed by potash, yielding potassium sulphide, potassium carbonate, and carbon tetrachloride :

$$2CSCl_2 + 3K_2O = 2K_2S + K_2CO_3 + CCl_4 .$$

Sulphur and Bromine.—Bromine dissolves sulphur, forming a brown red liquid probably containing a sulphur bromide analogous to sulphur monochloride ; but it has not been obtained pure.

Sulphur and Iodine.—These elements combine when heated together, even under water. The resulting compound, S_2I_2, containing 32 parts of sulphur and 127 parts of iodine, is a blackish-grey radio-crystalline mass, resembling native antimony sulphide. It decomposes at higher temperatures, gives off iodine on exposure to the air, and is insoluble in water. By heating 254 parts of iodine with 32 parts of sulphur, a compound is obtained which smells like iodine, and is said to be a powerful remedy in skin diseases. A cinnabar-red sulphur iodide is obtained, according to Grosourdi, by precipitating iodine trichloride with hydrogen sulphide.

SELENIUM.

Atomic weight, 79·4. Symbol, Se.

THIS is a very rare substance, much resembling sulphur in its chemical relations, and found in association with that element in some few localities, or replacing it in certain metallic combinations, as in the lead selenide of Clausthal in the Hartz. To separate it, the pulverised ore is treated with hydrochloric acid to dissolve earthy carbonates, and the washed and dried residue is ignited for some time with an equal quantity of black flux (a mixture of potassium carbonate and charcoal). The selenium is thereby converted into potassium selenide, which by treatment with boiling water is dissolved away from the oxides formed at the same time. This solution when exposed to the air absorbs oxygen, and yields the selenium as a grey deposit, which may be purified by washing, drying, and distillation.*

Selenium is a reddish-brown solid body, somewhat translucent, and having an imperfect metallic lustre. Its specific gravity, when rapidly cooled after fusion, is 4·3. At 100°, or a little above, it melts, and boils. It is insoluble in water, and exhales, when heated in the air, a peculiar and disagreeable odour, which has been compared to that of decaying horse-radish: it is insoluble in alcohol, but dissolves slightly in carbon bisulphide, from which solution it crystallises.

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* For further details, and for other methods, see Gmelin's Handbook of *Chemistry, English* Edition, vol. ii. p. 232.

Oxides of Selenium—Two oxides of selenium are known. The one containing the smallest proportion of oxygen is formed by the imperfect combustion of selenium in air or oxygen gas. It is a colourless gas which is the source of the peculiar horse-radish odour above mentioned. Its composition is not known.

The higher oxide, SeO_2, called selenious oxide, is produced by burning selenium in a stream of oxygen gas; it contains 79·4 parts, by weight, of selenium, and 32 of oxygen. It is a white solid substance which absorbs water rapidly, forming a hydroxide, viz.—

	Selenium.		Oxygen.		Hydrogen.		Selenious oxide.		Water.
Selenious acid, or Hydrogen selenite,	79·4	+	48	+	2	or	111·4	+	18

This acid, H_2SeO_3 or $H_2O.SeO_2$, analogous in composition and properties to sulphurous acid, is likewise produced by dissolving selenium in nitric or nitromuriatic acid. It is deposited from its hot aqueous solution by slow cooling in prismatic crystals like those of saltpetre ; but when the solution is evaporated to dryness, the selenious acid is resolved into water and selenious oxide, which sublimes at a higher temperature.

Selenious acid is a very powerful acid, approximating to sulphuric acid in the energy of its reactions. It reddens litmus, decomposes carbonates with effervescence, and decomposes nitrates and chlorides with aid of heat. Its solution precipitates lead and silver salts, and is decomposed by hydrogen sulphide, yielding a precipitate of selenium sulphide: $H_2SeO_3 + 2H_2S = 3H_2O + SeS_2$.

The metallic selenites resemble the sulphites. When heated with sodium carbonate in the inner blow-pipe flame, they emit the characteristic odour of selenium. They are not decomposed by boiling with hydrochloric acid.

Selenic acid, H_2SeO_4, is a more highly oxidised acid of selenium, analogous to sulphuric acid, and containing 79·4 parts, by weight, of selenium, 64 of oxygen, and 2 of hydrogen. The corresponding anhydrous oxide is not known. Selenic acid is prepared by fusing potassium or sodium nitrate with selenium, precipitating the selenate so produced with a lead salt, and then decomposing the compound with hydrogen sulphide. The acid strongly resembles oil of vitriol; but when very much concentrated, it is decomposed, by the application of heat, into selenious acid and oxygen. The selenates bear the closest analogy to the sulphates in almost every particular. They are decomposed by boiling with hydrochloric acid, chlorine being evolved and a salt of selenious acid being produced.

Hydrogen Selenide; *Selenhydric Acid; Seleniëtted Hydrogen*, H_2Se. —This substance is produced by the action of dilute sulphuric acid upon selenide of potassium or iron. It very much resembles sulphuretted hydrogen, being a colourless gas, freely soluble in water, and decomposing metallic solutions like that substance: insoluble selenides are thus produced. This gas is said to act very powerfully upon the lining membrane of the nose, exciting catarrhal symptoms, and destroying the sense of smell. It contains 79·4 parts selenium and 2 parts hydrogen.

TELLURIUM.

Atomic weight, 128. Symbol, Te.

THIS element possesses many of the characters of a metal, but it bears so close a resemblance to selenium, both in its physical properties and its chemical relations, that it is most appropriately placed in the same group with that body. Tellurium is found in a few scarce minerals, in association with gold, silver, lead, and bismuth, apparently replacing sulphur, and is most easily extracted from the bismuth sulpho-telluride of Chemnitz in Hungary. The finely-powdered ore is mixed with an equal weight of dry sodium carbonate, the mixture made into a paste with oil, and heated to whiteness in a closely covered crucible. Sodium telluride and sulphide are thereby produced, and metallic bismuth is set free. The fused mass is dissolved in water, and the solution freely exposed to the air, when the sodium and sulphur oxidise to sodium hydrate and thiosulphate, while the tellurium separates in the metallic state.

Tellurium has the colour and lustre of silver; by fusion and slow cooling it may be made to exhibit the form of rhombohedral crystals similar to those of antimony and arsenic. It is brittle, and a comparatively bad conductor of heat and electricity: it has a density of 6·26, melts at a little below a red-heat, and volatilises at a higher temperature. Tellurium burns when heated in the air, and is oxidised by nitric acid.

Tellurium forms two oxides, analogous in composition to the oxides of sulphur, and likewise forming acids by combination with water.

		Composition by weight.				
	Formula.	Hydrogen.		Tellurium.		Oxygen.
Tellurous oxide,	TeO_2			128	+	32
acid,	H_2TeO_3	2	+	128	+	48
Telluric oxide,	TeO_3			128	+	48
acid,	H_2TeO_4	2	+	128	+	64

Tellurous Oxide may be prepared by heating the precipitated acid to low redness. It also separates in semi-crystalline grains from the aqueous solution of the acid when gently heated; more abundantly and in well-defined octohedrons from the solution of tellurous acid in nitric acid. It is fusible and volatile, slightly soluble in water, but does not redden litmus. When fused with alkaline hydroxides or carbonates, it forms tellurites.

Tellurous Acid is best obtained by decomposing tellurium tetrachloride with water. It may also be prepared by dissolving tellurium in nitric acid of sp. gr. 1·25, and pouring the solution, after a few minutes, into a large quantity of water. By either process it is obtained as a somewhat bulky precipitate, which, when dried over oil of vitriol, appears as a light, white, earthy mass, having a bitter metallic taste. It is slightly soluble in water, more easily soluble in alkalis and acids, the nitric acid solution alone being unstable. Sulphurous acid, zinc, phosphorus, and other reducing agents, precipitate metallic tellurium from the acidified solution of tellurous acid. Like selenious acid, it is decomposed by hydrogen sulphide and alkaline hydrosulphides, with formation of a dark brown tellurium sulphide, which dissolves readily in excess of alkaline hydrosulphide, forming a sulpho-tellurite.

Tellurous acid is a hydroxide in which the acid and basic tendencies are nearly balanced; in other words, the tellurium of the compound can replace the hydrogen of an acid to form tellurous salts, and the hydrogen of the compound can be replaced by the basylous metals to form metallic tellurites.

TELLURIUM SALTS.	
$Te(SO_4)_2$	Sulphate.
$Te(NO_3)_4$	Nitrate.
$Te(C_2O_4)_2$	Oxalate.
$TeCl_4$	Chloride.

TELLURITES.	
H_2TeO_3	Hydrogen tellurite.
K_2TeO_3	Potassium tellurite.
$HKTeO_3$	Hydrogen and potassium tellurite.
$H_3K(TeO_3)_2$	Trihydropotassic tellurite.

The tellurites of potassium, sodium, barium, strontium, and calcium, are formed by fusing tellurous oxide or acid, with the carbonates of the several metals in the required proportions. These tellurites are all more or less soluble in water. The tellurites of the other metals, which are insoluble, are obtained by precipitation.

Telluric Oxide and Acid.—Equal parts of tellurous oxide and sodium carbonate are fused, and the product is dissolved in water; a little sodium hydrate is added, and a stream of chlorine passed through the solution. The liquid is next saturated with ammonia, and mixed with solution of barium chloride, by which a white insoluble precipitate of barium tellurate is thrown down. This is washed and digested with a quarter of its weight of sulphuric acid, and diluted with water. The filtered solution gives, on evaporation in the air, large crystals of telluric acid, which have the composition, $H_2TeO_4.2H_2O$.

Crystallised telluric acid is freely, although slowly, soluble in water: it has a metallic taste, and reddens litmus-paper. The crystals give off their water of crystallization at 100°, and the remaining acid, H_2TeO_4, when strongly heated, gives off more water, and yields the anhydrous oxide, TeO_3, which is then insoluble in water, and even in a boiling alkaline liquid. At the temperature of ignition, telluric oxide loses oxygen, and passes into tellurous oxide.

The tellurates of the alkali-metals are soluble in water, and are prepared by dissolving the required quantities of telluric acid and an alkaline carbonate in hot water. The other tellurates are insoluble, and are obtained by precipitation.

The composition of the alkaline tellurates is exhibited by the following formulæ:—

Neutral or Bipotassic tellurate, ...	K_2TeO_4	or $K_2O.TeO_3$
Acid or Hydro-potassic tellurate, ...	$HKTeO_4$	or $H_2O.K_2O.2TeO_3$
Quadracid or Trihydro-potassic tellurate, .	$HKTeO_4.H_2TeO_4$	or $3H_2O.K_2O.4TeO_3$
Anhydrous Quadritellurate, ...	$K_2TeO_4.3TeO_3$	or $K_2O.4TeO_3$

Tellurium Sulphides.—Tellurium forms two sulphides, TeS_2 and TeS_3, analogous in composition to the oxides; they are formed by the action of hydrogen sulphide on solutions of tellurous acid and telluric acid respectively. They are brown or black substances, which unite with metallic sulphides, forming salts called sulphotellurites and sulphotellurates.

Hydrogen Telluride, H_2Te.—*Tellurhydric Acid, Hydrotelluric Acid*, or *Telluretted Hydrogen.*—This compound is a gas, resembling sulphuretted and selenietted hydrogen. It is prepared by the action of hydrochloric acid on zinc telluride. It dissolves in water, forming a colourless liquid, which precipitates most metals from their solutions, and deposits tellurium on exposure to the air.

Tellurium Chlorides.—Tellurium forms a dichloride, $TeCl_2$, and a tetrachloride, $TeCl_4$, both volatile and decomposible by excess of water, the latter being completely resolved into tellurous and hydrochloric acids: $TeCl_4 + 3H_2O = 4HCl + H_2TeO_3$.

The tetrachloride unites with the chlorides of the alkali-metals, to form crystallisable double salts.

The *bromides* and *iodides of tellurium* correspond with the chlorides in properties and composition.

Compounds of the halogen-acids with tellurous oxide are also known. When this oxide is exposed to the action of gaseous *hydro-*

gen bromide in a vessel cooled to −14°, the compound $TeO_2.3HBr$ is formed in groups of small nearly black scales resembling iodine. At 40° this compound gives off HBr, and is reduced to $TeO_2.2HBr$, which, when heated to 300°, is resolved into water and a yellow oxybromide: $TeO_2.HBr = H_2O + TeOBr_2$; and at a still higher temperature this oxybromide is decomposed into the tetrabromide and tellurous oxide: $2TeOBr = TeBr_4 + TeO_2$. The tetrabromide passes off in black vapours and crystallises on cooling in dark brown needles.

Tellurous oxide is decomposed by *hydriodic acid* at ordinary temperatures, but absorbs it at −15°, forming a compound which decomposes as the temperature rises. Tellurous oxide likewise absorbs anhydrous *hydrofluoric acid.*

BORON.

Atomic weight, 11. Symbol, B.

THIS element, the basis of boric or boracic acid, is prepared by heating the double fluoride of boron and potassium with metallic potassium in a small iron vessel, and washing out the soluble salts with water. It is a dull, greenish-brown powder, which burns in the air when heated, producing boric oxide. Nitric acid, alkalis in the fused state, chlorine, and other agents, attack it readily.*

BORIC OXIDE AND ACID.—There is but one oxide of boron, namely, boric oxide, B_2O_3, containing 22 parts of boron and 48 of oxygen. It unites with water and metallic oxides, forming boric acid and metallic borates.

Boric or Boracic Acid, or *Hydrogen Borate*, H_3BO_3 or $3H_2O.B_2O_3$, contains 11 parts boron, 48 oxygen, and 3 hydrogen, or 70 parts boric oxide, and 54 water. It is found in solution in the water of the hot volcanic lagoons of Tuscany, whence a large supply is at present derived. It is also easily made by decomposing with sulphuric acid a hot solution of borax, which is an acid borate of sodium, occurring abundantly in certain salt lakes of India, Thibet, and other parts of Asia.

Boric acid crystallises in transparent colourless plates, soluble in about 25 parts of cold water, and in a much smaller quantity at the boiling heat; the acid has but little taste, and feebly affects vegetable colours. When heated, it loses water, and melts to a glassy transparent mass of anhydrous boric oxide, which dissolves many metallic oxides with great ease. The crystals dissolve in alcohol, and the solution burns with a green flame.

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* Wöhler and Deville, in 1858, by fusing boric oxide with aluminium, obtained very hard octohedral crystals and a graphite-like substance, which they regarded as modifications of boron analogous to the diamond and graphite varieties of carbon; but subsequent observations have shown that both these substances are compounds of boron and aluminium. (See ALUMINIUM.)

Glassy boric oxide in a state of fusion requires for its dissipation in vapour a very intense and long-continued heat; the aqueous solution cannot, however, be evaporated without very appreciable loss by volatilisation: hence it is probable that the acid is far more volatile than the anhydrous oxide.

Boron Nitride, BN.—This compound, containing 11 parts of boron and 14 of nitrogen, is produced by heating boric oxide with metallic cyanides, or by heating to bright redness a mixture of sal-ammoniac and pure anhydrous borax, or sodium biborate, $Na_2O.2B_2O_3$:

$$Na_2O.2B_2O_3 + 2NH_4Cl = 2BN + B_2O_3 + 2NaCl + 4H_2O.$$

It is a white amorphous powder, insoluble in water, infusible and non-volatile. When heated in a current of steam, it yields ammonia and boric oxide: $2BN+3H_2O=2NH_3+B_2O_3$, and likewise gives off a large quantity of ammonia when fused with potash.

Boron Chloride, BCl_3, was formerly believed to be a permanent gas; but recent researches have proved that it is a liquid, boiling at 17°, according to Wöhler and Deville, at 18°·23 under a pressure of 2760 millimeters (Regnault). It is decomposed by water, with production of boric and hydrochloric acids, and fuming strongly in the air. It is most easily obtained by exposing to the action of dry chlorine, at a very high temperature, an intimate mixture of glassy boric oxide and charcoal.

There is also a *Boron Bromide* of similar constitution.

Boron Fluoride, BF_3, is obtained by heating in a glass flask or retort 1 part of vitrified boric oxide, 2 of fluor-spar, and 12 of oil of vitriol. It is a transparent gas, very soluble in water, very heavy, and forming dense fumes in the air.

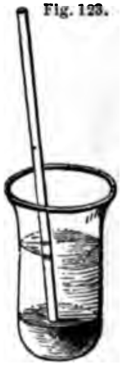
SILICON or SILICIUM.

Atomic weight, 28. Symbol, Si.

THIS element in union with oxygen constitutes silica or the earth of flints, in which form it enters largely into the composition of many of the rocks and mineral masses of which the surface of the earth is composed. The following process yields silicon most readily. The double fluoride of silicon and potassium is heated in a glass tube with nearly its own weight of metallic potassium; violent reaction ensues, and silicon is set free. When cold, the contents of the tube are put into cold water, which removes the saline matter and any residual potassium, and leaves the silicon untouched. So prepared, silicon is a dark-brown powder, destitute of lustre. Heated in the air, it burns, and becomes superficially converted into silica. It is also acted upon by sulphur and by chlorine. When silicon is strongly heated in a covered crucible, its properties are greatly changed; it becomes darker in colour, denser, and incombustible, refusing to burn even when heated by the flame of the oxy-hydrogen blowpipe.

Silicon, like carbon, is capable of existing in three different modifications. The modification above mentioned corresponds with the amorphous variety of carbon (lamp-black). The researches of Wöhler and Deville have established the existence of modifications corresponding with the diamond, and with the graphite variety of carbon. The diamond modification of silicon is most readily obtained by introducing into a red-hot crucible a mixture of 3 parts of potassium silico-fluoride, 1 part of sodium in small fragments, and 1 part of granulated zinc, and heating to perfect fusion. On slowly cooling, there is formed a button of zinc, covered and interspersed with needle-shaped crystals consisting of octohedrons joined in the direction of the axis. This crystallised silicon, which may be readily freed from zinc by treatment with acids, resembles crystallised hæmatite in colour and appearance: it scratches glass, and fuses at a temperature approaching the melting point of cast iron. The graphite modification of silicon is prepared by fusing, in a Hessian crucible, 5 parts of soluble glass (potassium silicate), 10 parts of cryolite (sodium and aluminium fluoride), and 1 part of aluminium. On treating the resulting button of aluminium with hydrochloric acid, the silicon remains in the form of scaly crystals, resembling graphite, but of somewhat brighter colour, scratching glass, like the previous modification. It is infusible. Its specific gravity is 2·49.

Fig. 123.



Silica, or **Silicic Oxide,** SiO_2.—This is the only known oxide; it contains 28 parts silicon and 32 parts oxygen. Colourless transparent rock-crystal consists of silica very nearly pure; common quartz, agate, chalcedony, flint, and several other minerals, are also chiefly composed of this substance.

The following experiment furnishes silica in a state of complete purity, and at the same time exhibits one of the most remarkable properties of silicon, namely, its attraction for fluorine. A mixture of equal parts of fluor-spar and glass, both finely powdered, is introduced into a glass flask, with a quantity of oil of vitriol. A tolerably wide bent tube, fitted to the flask by a cork, passes to the bottom of a glass jar (fig. 123), into which enough mercury is poured to cover the extremity of the tube. The jar is then half filled with water, and heat is applied to the flask.

The first effect is the disengagement of hydrofluoric acid: this substance, however, finding itself in contact with the silica of the powdered glass, undergoes decomposition, water and silicon fluoride being produced. The latter is a permanent gas, which escapes from the flask by the bent tube. By contact with a large quantity of water, it is in turn decomposed, yielding silica, which separates in a beautiful gelatinous condition, and an acid liquid, which is a double fluoride of silicon and hydrogen, $4HF.SiF_4$, commonly called hydrofluosilicic or silico-fluoric acid, thus

(1.) Reaction of hydrofluoric acid with silica:

$$4HF + SiO_2 = 2H_2O + SiF_4.$$

(2.) Decomposition of silicon fluoride by water:

$$2SiF_4 + 2H_2O = SiO_2 + 4HF.SiF_4.$$

The silica may be collected on a cloth-filter, well washed, dried, and heated to redness to expel water. The acid liquid is kept as a test for barium and potassium, with which it forms nearly insoluble precipitates, the double fluoride of silicon and potassium being used, as was stated, in the preparation of silicon.

Silicon fluoride, SiF_4, instead of being condensed into water, may be collected over mercury: it is a permanent gas, destitute of colour, and very heavy. Admitted into the air, it condenses the moisture of the latter, giving rise to a thick white cloud. It is important, in the experiment above described, to keep the end of the delivery-tube from touching the water of the jar, otherwise it almost instantly becomes stopped: the mercury effects this object.

Pure silica may also be prepared by another method, which is very instructive, inasmuch as it is the basis of the proceeding adopted in the analysis of all siliceous minerals. Powdered rock-crystal or fine sand is mixed with about three times its weight of dry sodium carbonate, and the mixture fused in a platinum crucible. When cold, the glassy mass is boiled with water, by which it is softened, and almost entirely dissolved. An excess of hydrochloric acid is then added to the filtered liquid, and the whole evaporated to complete dryness. By this treatment the gelatinous silica thrown down by the acid becomes completely insoluble, and remains behind when the dry saline mass is treated with acidulated water, by which the alkaline salts, alumina, ferric oxide, lime, and many other bodies which may happen to be present, are removed. The silica is washed, dried, and heated to redness.

The most prominent characters of silica are the following:—It is a very fine, white, tasteless powder, having a density of about 2·66, fusible only by the oxy-hydrogen blow-pipe. When once dried it is not sensibly soluble in water or dilute acids (with the exception of hydrofluoric acid). But on adding hydrochloric acid to a very dilute solution of potassium silicate, the liberated silica remains in solution. From this mixed solution of silica and potassium chloride, the latter may be separated by diffusion (comp. p. 146), whereby a moderately concentrated solution of silica in water is obtained. This solution has a distinctly acid reaction: it presents, however, but little stability. When kept for some time it gelatinises, the silica separating in the insoluble modification. The same effect is produced by the addition of a few drops of sulphuric or nitric acid, or of a solution of salt.

Silica is essentially an acid oxide, forming salts with basic metallic oxides, and decomposing all salts of volatile acids when heated with them. In strong alkaline liquids it is freely soluble. When heated with bases, especially those which are capable of undergoing fusion, it unites with them and forms salts, which are sometimes soluble in water, as in the case of the potassium and sodium silicates, when the proportion of base is considerable. Common glass is a mixture of several silicates, in which the reverse of this happens, the silica being in excess. Even glass, however, is slowly acted upon by water. Finely divided silica is highly useful in the manufacture of porcelain.

Silicon Hydride, or *Silicated Hydrogen*, was discovered by Buff and Wöhler, who obtained it by passing an electric current through a solution of sodium chloride, the positive pole employed consisting of aluminium containing silicon. More recently, Wöhler and Martius produced this gas by treating magnesium containing silicon with hydrochloric acid. Both methods yield silicic hydride mixed with free hydrogen. Friedel and Ladenburg, however, by decomposing silicic triethyl-formate (see SILICIC ETHERS) in contact with sodium, have obtained it pure, and shown that it consists of 28 parts by weight of silicon and 4 parts of hydrogen, answering to the formula SiH_4. The reaction by which it is produced is represented by the following equation:—

$$\underset{\text{Silicic triethyl formate.}}{4SiH(OC_2H_5)_3} = \underset{\text{Silicic hydride.}}{SiH_4} + \underset{\text{Tetrethylic silicate.}}{3Si(OC_2H_5)_4}.$$

Silicon hydride is a colourless gas. In the impure state, as obtained by the two processes above given, it takes fire spontaneously on coming in contact with the air, and burns with a white flame, evolving clouds of silica. Pure silicic hydride, however, does not ignite spontaneously under the ordinary atmospheric pressure; but on passing a bubble of air into the rarefied gas standing over mercury, it takes fire, and yields a deposit of amorphous silicon mixed with silica. On passing silicic hydride through a red-hot tube, it is decomposed, silicon being deposited.

COMPOUNDS OF SILICON AND CHLORINE.—Silicon unites directly with chlorine, forming a tetrachloride, $SiCl_4$. This compound is obtained by mixing finely divided silica with charcoal gelatinous silica.

When hydrochloric acid gas is passed over
heated to a temperature below redness, a very v
liquid is obtained, which, when purified by d
composition of *silicic hydrotrichloride*, $SiHCl_3$, c
silicon, 1 hydrogen, and 106·5 chlorine. This c
posed by water, forming a white oxygenated bo
hydrotrioxide, $Si_2H_2O_3$, which by prolonged con
further decomposed, with evolution of hydrogen
silica.

A mixture of silicic hydrotrichloride and
100° in a closed vessel becomes dark coloured, an
the *bromotrichloride*, $SiBrCl_3$.

Silicon tetrabromide, $SiBr_4$, obtained like
resembles that compound, but is less volatile.

Silicon Fluoride, SiF_4, has been already descri

PHOSPHORUS.

Atomic weight, 31. Symbol, P.

Phosphorus in the state of phosphoric acid i
ancient unstratified rocks and in lavas of moder
disintegrate and crumble down into fertile soil, t
into the organism of plants, and ultimately int
animals to which the plants serve for food. The

are conveyed to a chimney. This manufacture is now conducted on a very large scale, the consumption of phosphorus, for the apparently trifling article of instantaneous-light matches, being something prodigious.

Fig. 124.

Phosphorus, when pure, very much resembles in appearance imperfectly bleached wax, and is soft and flexible at common temperatures. Its density is 1·77, and that of its vapour 4·35, air being unity, or 62 referred to hydrogen as unity. It melts at 44°, and boils at 280°. On slowly cooling melted phosphorus, well-formed dodecahedrons are sometimes obtained. It is insoluble in water, and is usually kept immersed in that liquid, but dissolves in oil, in native naphtha, and especially in carbon bisulphide. When set on fire in the air, it burns with a bright flame, generating phosphoric oxide. Phosphorus is exceedingly inflammable; it sometimes takes fire by the heat of the hand, and demands great care in its management; a blow or hard rub will very often kindle it. A stick of phosphorus held in the air always appears to emit a whitish smoke, which in the dark is luminous. This effect is chiefly due to a slow combustion which the phosphorus undergoes by the oxygen of the air, and upon it depends one of the methods employed for the analysis of air, as already described. It is singular that the slow oxidation of phosphorus may be entirely prevented by the presence of a small quantity of olefiant gas, or the vapour of ether, or some essential oil; phosphorus may even be distilled in an atmosphere containing vapour of oil of turpentine in considerable quantity. Neither does the action go on in pure oxygen—at least, at the temperature of 15°·5, which is very remarkable; but if the gas be rarefied, or diluted with nitrogen, hydrogen, or carbonic acid, oxidation is set up.

A very remarkable modification of this element is known by the name of amorphous phosphorus. It was discovered by Schrötter, and may be made by exposing common phosphorus for fifty hours to a temperature of 240° to 250°, in an atmosphere which is unable to act chemically upon it. At this temperature it becomes red and opaque, and insoluble in carbon bisulphide, whereby it may be separated from ordinary phosphorus. It may be obtained in compact masses when common phosphorus is kept for a week at a constant high temperature. It is a coherent, reddish-brown, infusible substance, of specific gravity between 2·089 and 2·106. It does not become luminous in the dark until its temperature is raised to about 200°, nor has it any tendency to combine with the oxygen of the air. When heated to 260°, it is reconverted into ordinary phosphorus.

When phosphorus is melted beneath the surface of hot water, and a stream of oxygen gas forced upon it from a bladder, combustion ensues, and the phosphorus is converted in great part into a brick-red powder, which was formerly believed to be a peculiar oxide of phosphorus; but Schrötter has shown that it is a mixture, consisting chiefly of amorphous phosphorus.

Compounds of Phosphorus and Oxygen.

There are two definite oxides of phosphorus, in which the quantities of oxygen united with the same quantity of phosphorus are to one another as 3 to 5, viz.:—

		Composition by weight.		
	Formula.	Phosphorus.		Oxygen.
Phosphorus Trioxide, or Phosphorus oxide,	P_2O_3	62	+	48
Phosphorus Pentoxide, or Phosphoric oxide,	P_2O_5	62	+	80

Both these are acid oxides, uniting with water and metallic oxides to form salts, called **phosphites** and **phosphates** respectively; the hydrogen salts being also called phosphorous and phosphoric acid. There is also another oxygen-acid of phosphorus, containing a smaller proportion of oxygen, called hypophosphorous acid, to which there is no corresponding anhydrous oxide.

Hypophosphorous Acid, H_3PO_2.—When phosphorus is boiled with a solution of lime or baryta, water is decomposed, giving rise to phosphoretted hydrogen and hypophosphorous acid: the first escapes as gas, and the hypophosphorous acid remains as a barium salt:

$$P_8 + \underset{\substack{\text{Barium}\\ \text{hydroxide.}}}{3BaH_2O_2} + 6H_2O = \underset{\substack{\text{Barium}\\ \text{hypophosphite.}}}{3BaH_4(PO_2)_2} + \underset{\substack{\text{Hydrogen}\\ \text{phosphide.}}}{2H_3P}.$$

The soluble hypophosphite may be crystallised out by slow evaporation. On adding to the liquid the quantity of sulphuric acid necessary to precipitate the base, the hypophosphorous acid is obtained in solution, and may be reduced to a syrupy consistence by evaporation. The acid is very prone to absorb more oxygen, and is therefore a powerful deoxidising agent. All its salts are soluble in water.

Phosphorous Oxide, P_2O_3, is formed by the slow combustion of phosphorus in the air: or by burning that substance by means of a very limited supply of dry air, in which case it is anhydrous, and presents the aspect of a white powder. *Phosphorous acid*, H_3PO_3 or $3H_2O.P_2O_3$, is most conveniently prepared by adding water to the trichloride of phosphorus, when mutual decomposition takes place, the oxygen of the water being transferred to the phosphorus, generating phosphorous acid, and its hydrogen to the chlorine giving rise to hydrochloric acid :

$$PCl_3 + 3H_2O = 3HCl + H_3PO_3.$$

By evaporating the solution to the consistence of syrup, the hydrochloric acid is expelled, and the residue crystallises on cooling.

Phosphorous acid is very deliquescent, and very prone to attract oxygen and pass into phosphoric acid. When heated in a close vessel, it is resolved into phosphoric acid and pure phosphoretted hydrogen gas. It is composed of 110 parts of phosphorous oxide and 54 parts of water, or 31 phosphorus, 48 oxygen, and 3 hydrogen.

Phosphoric Oxide, P_2O_5 (also called *Anhydrous Phosphoric Acid*, or *Phosphoric Anhydride*).—When phosphorus is burned under a bell-jar by the aid of a copious supply of dry air, snowlike phosphoric oxide is produced in great quantity. This substance exhibits attraction for water, stronger even than that of sulphuric oxide; in fact sulphuric oxide may be prepared by heating strong sulphuric acid in contact with phosphoric oxide. Exposed to the air for a few moments, phosphoric oxide deliquesces to a liquid, and when thrown into water, combines with the latter with explosive violence, and is converted into phosphoric acid. The water thus taken up cannot again be separated.

When nitric acid of moderate strength is heated in a retort with which a receiver is connected, and fragments of phosphorus are added singly, taking care to suffer the violence of the action to subside after each addition, the phosphorus is oxidised to its maximum, and converted into phosphoric acid. By distilling off the greater part of the nitric acid, transferring the residue in the retort to a platinum vessel, and then cautiously raising the heat to redness, the phosphoric acid may be obtained pure. This is the *glacial phosphoric acid* of the Pharmacopœia.

A third method of preparing phosphoric acid consists in taking the acid calcium phosphate produced by the action of sulphuric acid on bone-earth, precipitating it with a slight excess of ammonia carbonate, separating by a filter the insoluble calcium salt, and then evaporating and igniting in a platinum vessel the mixed phosphate and sulphate of ammonia. Phosphoric acid alone remains behind. The acid thus obtained is somewhat impure.

One of the most advantageous methods of preparing pure phosphoric acid on the large scale, is to burn phosphorus in a two-necked glass globe through which a current of dry air is passed: in this way the process may be carried on continuously. The phosphoric oxide obtained may be preserved in that state, or converted into hydrate or glacial acid, by addition of water and subsequent fusion in a platinum vessel.

Glacial phosphoric acid, or metaphosphoric acid, is exceedingly

phosphorus with nitric acid, and by
on phosphorus pentachloride :

$$PCl_5 + 4H_2O = 5HCl + H_3P$$

The aqueous solution evaporated to a thin syr
of vitriol, deposits orthophosphoric acid in pris
same solution may be heated to 160° without
position of the acid ; but at 213° it gives off a mo
is converted into pyrophosphoric acid ; and at
off another molecule of water, and leaves m
Each of these acids forms a distinct class of salts,
peculiar to itself. They will be described in
general theory of saline compounds.

Phosphoric oxide is readily volatilised, and n
the heat of an ordinary spirit-lamp. The acid
platinum crucible at a red-heat ; at this tem
considerable quantities of vapour, but is still
point. Phosphoric acid is a very powerful acid :
than sulphuric acid, it expels the latter at hi
although it is displaced by sulphuric acid at com
Its solution has an intensely sour taste, and red
it is not poisonous.

Compounds of Phosphorus and Hyd

Phosphorus Trihydride.—*Phosphine.*—*Phos*
PH_3.—This body is analogous in some of its ch
ammoniacal gas ; its alkaline properties are, howe
It may be obtained in a state of purity by

extremity of the latter made to dip into the water of the pneumatic trough. In the reaction which ensues, the water is decomposed, and both its elements combine with the phosphorus.

$$P_8 + \underset{\substack{\text{Calcium}\\\text{hydroxide.}}}{3CaH_2O_2} + 6H_2O = 2PH_3 + \underset{\substack{\text{Calcium}\\\text{hypophosphite.}}}{3CaH_4P_2O_4}$$

The phosphoretted hydrogen prepared by the latter process has the singular property of spontaneous inflammability when admitted into the air or into oxygen gas; with the latter, the experiment is very beautiful, but requires caution: the bubbles should be admitted singly. When kept over water for some time, the gas loses this property, without otherwise suffering any appreciable change; but if dried by calcium chloride, it may be kept unaltered for a much longer time. Paul Thénard has shown that the spontaneous combustibility of the gas arises from the presence of the vapour of a liquid hydrogen phosphide, PH_2, which can be procured in small quantity, by conveying the gas produced by the action of water on calcium phosphide through a tube cooled by a freezing mixture. This substance forms a colourless liquid of high refractive power and very great volatility. It does not freeze at 0° F. (−17·8° C.) In contact with air it inflames instantly, and its vapour in very small quantity communicates spontaneous inflammability to pure phosphoretted hydrogen, and to all other combustible gases. It is decomposed by light into gaseous phosphoretted hydrogen, and a solid phosphide, P_2H, which is often seen on the inside of jars containing gas which, by exposure to light, has lost the property of spontaneous inflammation. Strong acids occasion its instantaneous decomposition. It is as unstable as hydrogen dioxide. It is to be observed that pure phosphoretted hydrogen gas itself becomes spontaneously inflammable if heated to the temperature of boiling water.

Phosphoretted hydrogen decomposes several metallic solutions, giving rise to precipitates of insoluble phosphides. With hydriodic acid it forms a crystalline compound, PH_4I, somewhat resembling sal-ammoniac.

Compounds of Phosphorus with Chlorine.

Phosphorus forms two chlorides, analogous in composition to the oxides, the quantities of chlorine combined with the same quantity of phosphorus being in the proportion of 3 to 5.

Phosphorus Trichloride, or **Phosphorous Chloride,** PCl_3, is prepared in the same manner as sulphur dichloride, by gently heating phosphorus in dry chlorine gas, the phosphorus being in excess; or by passing the vapour of phosphorus over fragments of calomel (mercurous chloride) contained in a glass tube, and strongly heated. It is a thin, colourless liquid, which fumes in the air, and has a powerful and offensive odour. Its specific gravity is 1·45. Thrown into water, it sinks to the bottom, and is slowly decomposed, yielding phosphorous acid and hydrochloric acid: $PCl_3 + 3H_2O = 3HCl + H_3PO_3$.

Phosphorus Pentachloride, or **Phosphoric Chloride,** PCl_5, is formed when phosphorus is burned in excess of chlorine. Pieces of phosphorus are introduced into a large tubulated retort, which is then filled with dry chlorine gas. The phosphorus takes fire, and burns with a pale flame, forming a white volatile crystalline sublimate, which is the pentachloride. It may be obtained in larger quantity by passing a stream of dry chlorine gas into the liquid trichloride, which becomes gradually converted into a solid crystalline mass. Phosphorus pentachloride is decomposed by water, yielding phosphoric and hydrochloric acids: $PCl_5+4H_2O=5HCl+H_3PO_4$.

Phosphorus Oxychloride, $POCl_3$, is produced, together with hydrochloric acid, when phosphorus pentachloride is heated with a quantity of water insufficient to convert it into phosphoric acid. It may also be prepared by distilling the pentachloride with dehydrated oxalic acid, or by distilling a mixture of phosphorus pentachloride and phosphoric oxide. It is a colourless liquid, of sp. gr. 1·7, possessing a very pungent odour, boiling at 110°, readily decomposed by water into hydrochloric and phosphoric acids.

A *sulphochloride* of analogous composition is produced by the action of hydrogen sulphide on the pentachloride. It is a colourless oily liquid, decomposed by water.

Two *bromides of phosphorus*, an *oxybromide*, and a *sulphobromide*, are known, corresponding in composition and properties with the chlorine compounds, and obtained by similar processes.

Phosphorus forms also two *iodides*, PI_2 and PI_3. Both are obtained by dissolving phosphorus and iodine together in carbon bisulphide, and cooling the liquid till crystals are deposited. Whatever proportions of iodine and phosphorus may be used, these two compounds always crystallise out, mixed with excess either of iodine or of phosphorus.

The *di-iodide* melts at 110°, forming a red liquid which condenses to a light red solid. The *tri-iodide* melts at 55°, and crystallises on cooling in well-defined prisms. Both are decomposed by water, yielding hydriodic and phosphorous acids, the di-iodide also depositing yellow flakes of phosphorus.

Compounds of Phosphorus with Sulphur and Selenium.

Sulphides.—When ordinary phosphorus and sulphur are heated together in the dry state, or melted together under water, combination takes place, attended with vivid combustion, and often with violent explosion. When amorphous phosphorus is used, the reaction *is not explosive,* though still very rapid.

Six compounds of sulphur and phosphorus have been prepared containing the following proportions of sulphur and phosphorus :—

	Composition by weight.		
	Phosphorus.		Sulphur.
Hemisulphide, P_4S,	31	+	8
Monosulphide, P_2S,	31	+	16
Sesquisulphide, P_4S_3,	31	+	24
Trisulphide, P_2S_3,	31	+	48
Pentasulphide, P_2S_5,	31	+	80
Dodecasulphide, P_2S_{12},	31	+	192

The fourth and fifth are analogous to phosphorous and phosphoric oxides respectively ; the others have no known analogues in the oxygen series. They may all be formed by heating the two bodies together in the required proportions ; but the trisulphide and pentasulphide are more easily prepared by warming the monosulphide with additional proportions of sulphur. Moreover, the two lower sulphides exhibit isomeric modifications, each being capable of existing as a colourless liquid and as a red solid.

The mono-, tri-, and pentasulphides of phosphorus unite with metallic sulphides, forming sulphur salts. The copper salts have the following composition :—

Hyposulphophosphite, $CuS.P_2S = CuP_2S_2$.
Sulphophosphite, $CuS.P_2S_3 = CuP_2S_4$.
Sulphophosphate, $CuS.P_2S_5 = CuP_2S_6$.

Selenides of Phosphorus, analogous in composition to the first, second, fourth, and fifth of the sulphides above mentioned, are produced by heating ordinary phosphorus and selenium together in the required proportions in a stream of hydrogen gas. The hemiselenide is a dark yellow, oily, fetid liquid, solidifying at 12° ; the other compounds are dark red solids. The mono-, tri-, and pentaselenides unite with metallic selenides, forming selenium-salts analogous to the sulphur-salts above mentioned.

BEFORE proceeding
it is advisable to enter more fully into the considerat
general laws of chemical combination, and certain theor
founded thereon, a sketch of which has already been
chapter on Oxygen (pp. 123–128).

The laws in question are: (1.) The Law of Equival
ing to which the replacement of elements one by an
takes place in definite proportion;—(2.) The Law of
according to which the several quantities of an elem
can unite with a fixed quantity of another element
one another, for the most part, in simple numerical prop
observation of these laws has led to the idea that t
bodies are made up of indivisible particles called atom
a constant weight peculiar to itself; and that chemical
takes place by the juxtaposition of these atoms, 1 to 1,
2 to 3, &c., a group of atoms thus united being called
This is the atomic hypothesis of Dalton.

Equivalents.—The equivalent weight of an ele
compared with that of hydrogen, taken as unity,
cases be determined by direct substitution. Thus,
dissolves in hydrochloric or sulphuric acid, the qu
metal which takes the place of 1 part by weight of h
equivalent weight. In this manner it is found that
of sodium is 23, of zinc 32·6, of magnesium 12, &c.
organic compounds—acetic acid, for example—are a
chlorine and bromine in such a manner that 1 part of
is removed and its place supplied by chlorine or bro
ounce, &c.) of hydrogen thus

weights of elements may be determined without recourse to direct substitution, which is not always practicable.

The left hand column of the following table contains a list of those metallic or basylous elements which unite in one proportion only with the four non-metallic or chlorous elements in the right hand column, the numbers opposite to each element showing the proportions in which the combination takes place (*e.g.* 12 magnesium with 35·4 chlorine, 39·1 potassium with 80 bromine, &c.), or, in other words, the equivalent weights.

	Equiv.		Equiv.
Hydrogen	1	Fluorine	19
Beryllium	4·7	Chlorine	35·4
Aluminium	3·13	Bromine	80
Lithium	7	Iodine	127
Magnesium	12		
Calcium	20		
Sodium	23		
Zinc	32·6		
Indium	37·7		
Potassium	39·1		
Strontium	43·8		
Barium	68·7		
Rubidium	85·4		
Cæsium	133		

These numbers, as will be explained further on, are also the relative quantities of the several elements which would be separated from their compounds by an electric current of given strength: thus, if the same current were passed through solutions of sodium bromide, potassium iodide, and zinc chloride, the quantities of sodium, potassium, zinc, bromine, iodine, and chlorine simultaneously separated would be to one another in the proportion of the numbers in the table.

In most cases, however, combination between two elements takes place in more than one proportion, and in such cases the notion of equivalent value becomes less definite; in fact, such elements may be said to have as many equivalent weights as there are ways in which they can combine with others. Thus, tin forms two series of compounds, the stannous compounds, in which 59 parts of the metal unite with 35·5 of chlorine, 80 of bromine, 127 of iodine, &c., and the stannic compounds, in which half that quantity of tin, viz., 29·5 parts, discharges the same function; tin has therefore two equivalents, viz., 59 in the stannous and 29·5 in the stannic compounds. In like manner, the equivalent of iron is 28 in the ferrous and 18⅔ in the ferric compounds.*

---

* In such cases it is sometimes supposed that the two classes of compounds contain different metallic radicles, combined with the same quantity of a non-metallic or chlorous element, the stannous compounds, for example, being supposed to contain a radicle called *stannosum* (eq. 59), and the stannic compounds another radicle called *stannicum* (eq. 29·5). This, however, is a mere

of the metal ; thus 3
acid (=1 part hydrogen + 35·5 chlorine) and :
of free hydrogen and 23 + 35·5 (=58·5) sodiun
such thing as the expulsion of part of the hydı
of a compound containing both hydrogen and
with the chlorine.

With water, however, the case is differen
thrown upon water, 18 parts of that compou
16 oxygen) are decomposed, in such a manner t
gen is expelled by an equivalent quantity
sodium hydroxide is formed, containing—

Sodium.		**Hydrogen.**		**Oxy**
23	+	1	+	1

This compound remains in the solid state
evaporated to dryness ; and if it be further hea
sodium, the remaining half of the hydrogen
anhydrous sodium-oxide remains, composed of
16 oxygen.

Water differs, therefore, from hydrochloric ac
that its hydrogen may be replaced by sodium in
yielding successively a hydroxide and an anhydr
tions of which to the original compound ma
sented :—

Water.			**Sodiumhydroxide.**	
Hydrogen.	**Ox.**	**Hyd.**	**Sod.**	**Ox.**
(1+1) +	16			

The weights of the three atoms concerned in this reaction are to one another in the same proportion as the equivalent weights, or, taking the hydrogen as the unit in each case, we may say that the atomic weights of sodium and chlorine are identical with their equivalent weights.

(2.) Each molecule of water must be supposed to contain two atoms of hydrogen: for if it contained only one atom, then since the first action of the sodium is to expel only half the hydrogen, it would follow that each atom of hydrogen would be split into two, and that each molecule of sodium hydroxide would contain only half an atom of hydrogen; this, however, is at variance with the fundamental notion of atoms, namely, that they are indivisible. These two atoms of hydrogen are combined with a quantity of oxygen weighing 16, which is therefore the smallest quantity of oxygen capable of entering into the reaction under consideration:

$$\begin{array}{cccccccccc} \mathrm{H} & \mathrm{H} & \mathrm{O} & + & \mathrm{Na} & = & \mathrm{H} & \mathrm{Na} & \mathrm{O} & + & \mathrm{H} \\ 1 & 1 & 16 & & 23 & & 1 & 23 & 16 & & 1 \end{array}$$

and we shall hereafter find that the same is true with regard to all other well-defined reactions in which oxygen takes part. Hence this quantity of oxygen, 16 parts by weight (hydrogen being the unit), is regarded as the weight of the atom of oxygen.

This atomic weight of oxygen is not equal to the equivalent weight, as in the case of chlorine, but *twice as great*, 8 parts of oxygen being the quantity which is capable of replacing one part of hydrogen in combination, and may in many cases be directly substituted for it, as when alcohol, a compound of 12 parts carbon, 3 hydrogen, and 8 oxygen, is oxidised to acetic acid containing 12 carbon, 2 hydrogen, and 16 oxygen.

Let us now consider the hydrogen-compound of nitrogen, that is to say, *ammonia*. This is composed of 1 part of hydrogen united with $4\frac{2}{3}$ or $\frac{14}{3}$ of nitrogen. Now in this compound the hydrogen is replaceable by thirds, or 3 parts hydrogen with 14 parts nitrogen. When potassium is heated in ammonia gas, a compound called potassamine is formed, in which one-third of the hydrogen is replaced by potassium. Another compound, called tripotassamine, is also known, consisting of ammonia in which the whole of the hydrogen is replaced by an equivalent quantity of potassium.

There is also a large class of compounds derived from ammonia in like manner by the replacement of $\frac{1}{3}$, $\frac{2}{3}$, or the whole of the hydrogen by equivalent quantities of certain groups of elements called *compound radicles* (see page 276). Hence, by reasoning similar to that which was above applied to water, it is inferred that the molecule of ammonia contains 3 atoms of hydrogen, and that the atomic weight of nitrogen is 14. Moreover, in certain organic compounds this quantity of nitrogen may be substituted for 3 parts of hydrogen, or $\frac{14}{3}$ nitrogen for 1 hydrogen; consequently the atomic weight of nitrogen is *three* times its equivalent weight.

Next take the case of *marsh gas* or *methane*, a compound of 1 part hydrogen with 3 parts carbon, or 4 of hydrogen with 12 of carbon. When this gas is mixed with chlorine, and exposed to diffuse daylight, a new compound is formed, in which one-fourth of the hydrogen belonging to the marsh gas is replaced by an equivalent quantity of chlorine ; and if the chlorine is in excess, and the mixture exposed to sunshine, three other compounds are formed, in which one-half, three-fourths, and all the hydrogen, are thus replaced. The results may be thus expressed :—

Methane.

$$\overset{\text{Carbon.}}{12} + \overbrace{1 + 1 + 1 + 1}^{\text{Hydrogen.}}$$

Chloromethane.

$$\overset{\text{Carbon.}}{12} + \overbrace{1 + 1 + 1}^{\text{Hydrogen.}} + \overset{\text{Chlorine.}}{35{\cdot}5}$$

Dichloromethane.

$$\overset{\text{Carbon.}}{12} + \overbrace{1 + 1}^{\text{Hydrogen.}} + \overbrace{35{\cdot}5 + 35{\cdot}5}^{\text{Chlorine.}}$$

Trichloromethane or Chloroform.

$$\overset{\text{Carb.}}{12} + \overset{\text{Hyd.}}{1} + \overbrace{35{\cdot}5 + 35{\cdot}5 + 35{\cdot}5}^{\text{Chlorine.}}$$

Tetrachloromethane.

$$\overset{\text{Carbon.}}{12} + \overbrace{35{\cdot}5 + 35{\cdot}5 + 35{\cdot}5 + 35{\cdot}5}^{\text{Chlorine.}}$$

Hence, by reasoning similar to the above, it is inferred that the molecule of methane contains 4 atoms of hydrogen, and that the atomic weight of carbon is 12. Moreover, as this quantity of carbon can unite with 4 × 35·5 parts, or 4 atoms of chlorine, it follows that the atomic weight of carbon is equal to four times its equivalent weight.

We have thus shown in three cases how the atomic weight of an element may be determined by the proportion in which equivalent substitution takes place in its compounds with hydrogen. Sulphur, selenium, and tellurium, form hydrogen-compounds exactly analogous in this respect to water, the hydrogen being replaceable by halves ; their atomic weights are therefore double of their equivalent weights.

Silicon forms with chlorine a compound containing 7 parts silicon with 35·5 parts chlorine; and in this one-fourth of the chlorine is replaceable by hydrogen or by bromine: hence the atomic weight of silicon is, like that of carbon, equal to four times the equivalent weight, its numerical value being 28. There are also some elements in which the atomic weight is equal to five times, others in which it is equal to six times, and others in which it is perhaps equal to seven times or eight times the equivalent weight: higher ratios have not been observed.

It must not be supposed that the atomic weights of elementary bodies are always actually determined in the manner above described. There are several other methods of determining their numerical values, as will be presently explained; and the values obtained by different methods do not always exhibit exact agreement; but the atomic weights of all the more important elements may be regarded as definitely fixed within small numerical errors. The equivalent value of an element, or the ratio of the equivalent to the atomic weight, is also subject to some variation, as will be presently explained, according to the view which may be taken of the constitution of particular compounds.

The values of the atomic weights on which chemists are now, for the most part, agreed, are given in the table on page 3.

Physical and Chemical Relations of Atomic Weights.

The atomic weights of the elementary bodies exhibit some remarkable relations to their physical properties, and to the proportions in which they unite by volume.

1. **To the Specific Heats of the Elementary Bodies.**—Dulong and Petit, in the course of their investigations on specific heat, observed that, if the specific heats of bodies be computed upon equal weights, numbers are obtained all different, and exhibiting no simple relations amongst themselves; but if, instead of equal weights, quantities be taken in the proportion of the atomic weights, the resulting specific heats come out very nearly equal, at least in the case of solid and liquid elements, showing that some exceedingly intimate connection must exist between the relation of bodies to heat, and their chemical nature.

In the following table, the solid and liquid elementary bodies are arranged in the order of their specific heats, as determined by Regnault, beginning with those whose specific heat is the greatest; and this order, it will be observed, is the inverse of that of the atomic weights in the third column:—

Specific Heats of Elementary Bodies.

Elements.	Specific Heat (that of Water = 1.)	Atomic Weights.	Product of Sp. Heat × At. Weight.
Lithium,	0·9408	7	6·59
Sodium,	0·2934	23	6·75
Aluminium,	0·2143	27·4	5·89
Phosphorus { liquid,	0·2120	31	6·57
Phosphorus { solid,	0·1887		5·85
Sulphur,	0·2026	32	6·48
Potassium,	0·1696	39	6·61
Iron,	0·1138	56	6·37
Nickel,	0·1086	58·8	6·37
Cobalt,	0·1070	58·8	6·28
Copper,	0·0952	63·4	6·04
Zinc,	0·0956	65·2	6·24
Arsenic,	0·0814	75	6·10
Selenium,	0·0762	79·4	6·02
Bromine (solid),	0·0843	80	6·75
Palladium,	0·0593	106·6	6·31
Silver,	0·0570	108	6·16
Cadmium,	0·0567	112	6·35
Indium,	0·0570	113·4	6·46
Tin,	0·0562	118	6·63
Antimony,	0·0508	122	6·19
Iodine,	0·0541	127	6·87
Tellurium,	0·0474	128	6·06
Gold,	0·0324	197	6·38
Platinum,	0·0311	197·4	6·15
Mercury { solid,	0·0319	200	6·38
Mercury { liquid,	0·0833		6·66
Thallium,	0·0335	204	6·83
Lead,	0·0314	207	6·50
Bismuth,	0·0308	210	6·48

A comparison of the numbers in the fourth column of this table shows that, for a considerable number of elementary bodies in the solid state, the specific heats are very nearly proportional to the atomic weights, so that the products of the specific heats of the elements into their atomic weights give nearly a constant quantity, the mean value being 6·4. This quantity may be taken to represent the *atomic heat* of the several elements in the solid state, or the quantity of heat which must be imparted to or removed from atomic proportions of the several elements, in order to produce equal variations of temperature.

Carbon, boron, and silicon were formerly regarded as exceptions to this law, their atomic heats, calculated from the specific heats determined at ordinary temperatures, being considerably below the mean value of those of the other elements, as shown by the following table:—

Elements.		Specific Heat.	Atomic Weights.	Product of Sp. Heat × At. Weight.
Boron, ...		0·2500	11	2·75
Carbon	wood charcoal, .	0·2415	12	2·90
	graphite, . .	0·2008		2·41
	diamond, . .	0·1469		1·76
Silicon	crystallised, .	0·1774	28	4·97
	fused, . .	0·1750		4·70

F. Weber has, however, lately shown * that the specific heats of these three bodies increase rapidly at higher temperatures, and that at particular temperatures (about 600° for carbon) they become constant, giving for the atomic heats a mean value of about 6, which is nearly the same as that of other elements of small atomic weight, like aluminium and phosphorus, thus:—

	Sp. Heat.	At. Weight.	At. Heat.
Silicon, . .	0·203	28	5·7
Carbon, . .	0·467	12	5·6
Boron, . . .	0·5	11	5·5

The specific heats and molecular weights of similarly constituted compounds exhibit, for the most part, the same relation as that which is observed between the specific heats and atomic weights of the elements.

2. **To the Crystalline Forms of Compounds.**—It is found that, in many cases, two or more compounds which, from chemical considerations, are supposed to contain equal numbers of atoms of their respective elements, crystallise in the same or in very similar forms. Such compounds are said to be *isomorphous*.† Thus the sulphates constituted like magnesium sulphate, $MgSO_4 + 7H_2O$, are isomorphous with the corresponding selenates, $MgSeO_4 + 7H_2O$.

Accordingly, these isomorphous relations are often appealed to for the purpose of fixing the constitution of compounds, and thence deducing the atomic weights of their elements, in cases which would otherwise be doubtful. Thus aluminium forms only one oxide, viz., alumina, which is composed of 18·3 parts by weight of aluminium and 16 parts of oxygen. What, then, is the atomic weight of aluminium? The answer to this question will depend upon the constitution assigned to alumina, whether it is a monoxide, sesquioxide, dioxide, &c. Thus:—

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* Ann. Chim. Phys. [5]. viii. 132.

† Ἴσος, equal; μορφή, form.

			O.		Al.
Monoxide	**AlO**	=	**16**	+	**18·3**
Sesquioxide	Al_2O_3	=	48	+	27·4 27·4
Dioxide	AlO_2	=	32	+	36·6
Trioxide	AlO_3	=	48	+	54·8

The numbers in the last column of this table are the weights which must be assigned to the atom of aluminium, according to the several modes of constitution indicated in the first column; but there is nothing in the constitution of the oxide itself that can enable us to decide between them. Now, iron forms two oxides, in which the quantities of oxygen united with the same quantity of iron are to one another as 1 : 1½, or as 2 : 3. These are therefore regarded as monoxide, FeO, and sesquioxide, Fe_2O_3, and this last oxide is known to be isomorphous with alumina. Consequently alumina is also regarded as a sesquioxide, Al_2O_3, and the atomic weight of aluminium is inferred to be 27·4.

3. To the Volume-relations of Elements and Compounds.— The atomic weights of those elements which are known to exist in the state of gas or vapour are, with one or two exceptions, proportional to their specific gravities in the same state. Taking the specific gravity of hydrogen as unity, those of the following gases and vapours are expressed by numbers identical with their atomic weights:—

Hydrogen	1	Oxygen	16
Chlorine	35·5	Sulphur	32
Bromine	80	Selenium	79
Iodine	127	Tellurium	128

The exceptions to this rule are exhibited by *phosphorus* and *arsenic*, whose vapour-densities are twice as great as their atomic weights, that of phosphorus being 62, and that of arsenic 150; and by *mercury* and *cadmium*, whose vapour-densities are the halves of their atomic weights, that of mercury being 100, and that of cadmium 56.

From these relations, considered in connection with above explained laws of combination by weight, it follows that the volumes of any two elementary gases which make up a compound molecule, are to one another in the same ratio as the numbers of atoms of the same elements which enter into the compound, excepting in the case of phosphorus and arsenic, for which the number of volumes thus determined has to be halved, and of mercury and cadmium, for which it must be doubled; thus—

The molecule	HCl	contains		1	vol.	H	and	1	vol.	Cl
,,	H_2O	,,		2	,,	H	,,	1	,,	O
,,	H_3N	,,		3	,,	H	,,	1	,,	N
,,	H_3P	,,		3	,,	H	,,	$\frac{1}{2}$	,,	P
			or	6	,,	H	,,	1	,,	P
,,	Cl_3As	,,		3	,,	Cl	,,	$\frac{1}{2}$	,,	As
			or	6	,,	Cl	,,	1	,,	As
,,	Cl_2Hg	,,		2	,,	Cl	,,	2	,,	Hg

If the smallest volume of a gaseous element that can enter into combination be called the combining volume of that element, the law of combination may be expressed as follows:—*The combining volumes of all elementary gases are equal, excepting those of phosphorus and arsenic, which are only half those of the other elements in the gaseous state, and those of mercury and cadmium, which are double those of the other elements.*

It appears, then, that in all cases the volumes in which gaseous elements combine together may be expressed by very simple numbers. This is the "Law of Volumes," first observed by Humboldt and Gay-Lussac in 1805, with regard to the combination of oxygen and hydrogen, and afterwards established in other cases by Gay-Lussac, whose observations, published in his "Theory of Volumes," afforded new and independent evidence of the combination of bodies in definite and multiple proportions, in corroboration of that derived from the previously observed proportions of combination by weight.

Gay-Lussac likewise observed that the product of the union of two gases, when itself a gas, sometimes retains the original volume of its constituents, no contraction or change of volume resulting from the combination, but that when contraction takes place, which is the most common case, the volume of the compound gas always bears a simple ratio to the volumes of its elements: and subsequent observation, extended over a very large number of compounds, organic as well as inorganic, has shown that, with a few exceptions, probably only apparent, *the molecules of compound bodies in the gaseous state occupy twice the volume of an atom of hydrogen gas.* No matter what may be the number of atoms or volumes that enter into the compound, they all become condensed into two volumes; thus—

1	vol.	H	and	1	vol.	Cl	form	2	vol.	HCl,	hydrochloric acid.
1	,,	N	,,	1	,,	O	,,	2	,,	NO,	nitrogen dioxide.
2	,,	H	,,	1	,,	O	,,	2	,,	H_2O,	water.
3	,,	H	,,	1	,,	N	,,	2	,,	H_3N,	ammonia.
3	,,	H	,,	$\frac{1}{2}$	,,	P	,,	2	,,	H_3P,	hydrogen phosphide.

Similarly in the union of compound gases, *e.g.*,

1	vol.	ethyl,	C_2H_5,	and	1	vol.	Cl.	form	2	vol.	C_2H_5Cl, ethyl chloride.
2	,,	ethyl,	C_2H_5,	,,	1	,,	O	,,	2	,,	$(C_2H_5)_2O$, ethyl oxide.
2	,,	ethene,	C_2H_4,	,,	2	,,	Cl	,,	2	,,	$C_2H_4Cl_2$, ethene chloride.
2	,,	ethene,	C_2H_4,	,,	1	,,	O	,,	2	,,	C_2H_4O, ethene oxide.

It will presently be shown, as at least highly probable, that the molecule of an elementary gas in the free state is made up of two atoms, HH for example. The law just enunciated may therefore be generalised as follows. *The molecules of all gases, simple or compound, occupy equal volumes*; or, *equal volumes of all gases contain equal numbers of molecules.*

This is called the "Law of Avogadro," having been first enunciated (in 1811) by an Italian physicist of that name. It is quite in accordance with the observed fact that all perfect gases, simple and compound, are equally affected by equal variations of pressure and temperature; and indeed it may be shown, by mathematical reasoning, to follow as a necessary consequence from the physical constitution of gases as explained in connection with the dynamical theory of heat (pp. 65–69): but the demonstration is not of a nature adapted for an elementary book. The law may, however, be considered as completely established by the relations between the combining proportions of the elements by weight and by volume as already explained, and it is now regarded as affording the surest method of fixing the molecular constitution of all compounds that can be obtained in the gaseous state, and the atomic weights of the elements contained in them.

Suppose, for example, it were required to determine the atomic weight of tin. This metal forms a volatile chloride (stannic chloride), in which 29·5 parts by weight of tin are combined with 35·5 parts of chlorine: 29·5 is therefore the equivalent of tin in this compound. Now the vapour-density of this chloride, or the weight of one volume referred to hydrogen as unity, is 135; consequently the weight of two volumes of the vapour is 270, and this contains 118 parts of tin and 4 × 35·5 or 142 of chlorine; and as this appears to be the chloride containing the largest proportion of chlorine, or the smallest proportion of tin, it is regarded as a compound of 4 atoms of chlorine and 1 atom of tin, and the atomic weight of tin is thus found to be 118.

When an element does not form any volatile compounds whose vapour-densities can be exactly ascertained, its atomic weight may be determined by its specific heat, according to the law of Dulong and Petit (p. 247), or by its isomorphous relations with other elements, as already explained in the case of aluminium. To give an instance of the determination of the atomic weight of an element according to its specific heat, we may take the case of indium. This metal forms a chloride containing 35·5 parts of chlorine and 37·8 parts of indium, which latter number is therefore the equivalent weight of the metal. Now when indium was first discovered (in 1863), this chloride was, for reasons which need not here be specified, regarded as a dichloride, $InCl_2$, and consequently the atomic weight of indium was supposed to be 75·6. Subsequently, however, Bunsen showed that the specific heat of indium, referred to the unit of weight, is 0·057, and this number multiplied by 75·6 gives for the atomic heat the number 4·5, which does not agree with the law of Dulong and

Petit; but if the chloride be regarded as a trichloride, MCl_3, making the atomic weight of the metal equal to three times its equivalent weight, or 113·4, the atomic heat becomes 6·15, which agrees very nearly with the general law. This number 113·4 is therefore now adopted as the atomic weight of indium.

Specific or Atomic Volume.

These terms denote the quotient obtained by dividing the molecular weight of a body by its specific gravity. Now from the law of condensation in the combination of gases above detailed (p. 251) it follows that *the specific gravity of any compound gas or vapour, referred to hydrogen as unity, is equal to half its atomic or molecular weight*: hence also, *the specific volumes of compound gases or vapours referred to that of hydrogen as unity are, with a few exceptions, equal to* 2. It will presently be shown that the same law applies to the specific volumes of the elementary gases themselves.

Some compounds, however, exhibit a departure from this rule, their observed specific gravities being equal to only one-fourth their molecular weights, or their molecules occupying four times the volume of an atom of hydrogen. Such is the case with sal-ammoniac, NH_4Cl, phosphorus pentachloride, PCl_5, sulphuric acid, H_2SO_4, ammonium hydrosulphide $(NH_4)SH$, and a few others. This anomaly is probably due, in some cases at least, to a decomposition or "dissociation" of the compound at the high temperature to which it is subjected for the determination of its vapour-density; NH_4Cl, for example, splitting up into NH_3 and HCl, each of which occupies two volumes, and the whole therefore four volumes; and in like manner H_2SO_4 may be supposed to separate into H_2O and SO_3; PCl_5 into PCl_3 and Cl_2; $(NH_4)SH$ into NH_3 and H_2S, &c.

On the other hand, some substances, both simple and compound, exhibit, at temperatures not far above their boiling points, vapour-densities considerably greater than they should have according to the general law, whereas when raised to higher temperatures they exhibit normal vapour-densities. Thus sulphur, which boils at 440°, exhibits at 1000°, like elementary gases in general, a vapour-density equal to its atomic weight, viz., 32; but at 500° its vapour-density is nearly three times as great. Again, acetic acid, $C_2H_4O_2$, whose molecular weight is $24+4+16=60$, has, at temperatures considerably above its boiling point, a vapour-density nearly equal to 30; but at 125° (8 degrees above its boiling point), its vapour-density is rather more than 45, or 1½ times as great. This anomalous increase of vapour-density appears to take place when the substance approaches its liquefying point, at which also it exhibits irregularities in its rate of expansion and contraction by variations of pressure and temperature—at which, in short, it begins to behave itself like a liquid; but at higher temperatures it exhibits the physical characters of a perfect gas, and then also its specific gravity becomes normal.

Specific Volumes of Liquids and Solids.—The following table exhibits the specific volumes of those solid and liquid elements whose specific gravities have been determined with sufficient accuracy. The elements are arranged in the order of their specific volumes, beginning with the smallest.

Specific Volumes of Solid and Liquid Elements.

	Atomic Weight.	Specific Gravity.	Specific Volume.
Carbon, as *diamond*, .	12	3·52	3·4
Beryllium, .	9·4	2·1	4·4
Carbon, as *graphite*, .	12	2·3	5·2
Nickel, . .	58·8	8·6	6·8
Manganese,	55	8·03	6·85
Cobalt, . .	58·8	8·50	7·0
Iron, . .	56	7·8	7·2
Copper, .	63·4	8·95	7·2
Chromium,	52·2	7·01	7·4
Iridium, .	198	21·8	9·1
Platinum, .	197·4	21·5	9·2
Zinc, . .	65·2	7·1	9·2
Palladium, .	106·6	11·8	9·2
Rhodium, .	104·4	11·0	9·4
Silver, . .	108	10·5	10·2
Gold, . .	199	19·34	10·2
Aluminium,	27·4	2·67	10·26
Molybdenum, . .	96	8·6	11·1
Silicon, *graphitoïdal*,	28	2·5	11·2
Lithium, .	7	0·59	11·9
Cadmium, .	112	8·7	13·0
Uranium, .	240	18·4	13·2
Arsenic, .	75	5·63	13·3
Magnesium, . .	24	1·74	13·8
Mercury, *liquid*, .	200	14·8	14·8
Sulphur, *trimetric*, .	32	2·07	15·2
Indium, .	113·4	7·4	15·3
Phosphorus, *red*, . .	31	1·94	15·8
Sulphur, *monoclinic*,	32	1·98	16·2
Tin, . . .	118	7·3	16·2
Selenium, *granular*,	79·4	4·80	16·4
Phosphorus, *yellow*,	31	1·84	16·8
Antimony, .	122	6·7	18·2
Lead, . .	207	11·33	18·3
Selenium, *amorphous*,	79·4	4·28	18·4
Tellurium, .	128	6·2	20·6
Bismuth, .	210	9·8	21·2
Sodium, .	23	0·97	23·7
Calcium, .	40	1·58	25
Iodine, . .	127	4·95	25·7
Bromine, *liquid*, .	80	3·19	25·8
Chlorine, *liquid*, .	35·5	1·33	26·7
Strontium,	87·6	2·54	34·4
Potassium, .	39·1	0·86	45·6

The numbers in the third column of this table do not exhibit the simplicity of relation which exists between the specific volumes of gaseous bodies. There are, indeed, several causes which interfere with the existence, or at least with the observation, of such simple relations between the specific volumes of solid and liquid elements. In the first place, the densities of three of them, viz., mercury, bromine, and chlorine, are such as belong to them in the liquid state, *whereas the* densities assigned to all the others have been determined in the solid state. In solids, moreover, the density is greatly affected by the state of aggregation, whether crystalline or amorphous, and in dimorphous bodies, each form has a density peculiar to itself. Further, as solids and liquids are variously affected by heat, each having a peculiar rate of expansion, and that rate being different at different temperatures, it is not to be expected that their specific volumes should exhibit simple relations, unless they are compared at temperatures at which they are similarly affected by heat. Even gases are found to exhibit abnormal specific volumes if compared at temperatures too near the points at which they pass into the liquid state. In liquids, the simplest relations of specific volume are found at those temperatures for which the tensions of the vapours are equal (Kopp); and in solids, the melting points are most probably the comparable temperatures. Now the specific gravities of most of the solid elements in the preceding table have been determined at mean temperatures (as at 15°·5), which, in the case of potassium, sodium, phosphorus, and a few others, do not differ greatly from the melting points, but in other cases, as with gold, platinum, iron, &c., are removed from the melting points by very long intervals. In spite, however, of these causes of divergence, the specific volumes of certain analogous elements are very nearly equal to each other: viz., those of selenium and sulphur; of chromium, iron, cobalt, copper, manganese, and nickel; of molybdenum and tungsten; of iridium, platinum, palladium, and rhodium; and of gold and silver.

Specific Volumes of Solid and Liquid Compounds. The most general relation that has been observed between the specific volumes of solid compounds, is that *isomorphous compounds have equal specific volumes*, in other words, that their densities are proportional to their molecular weights: such is the case, for example, with the native carbonates of strontium (strontianite) and of lead (cerussite):

Formula.	Molecular weight.	Specific gravity.	Specific volume.
$SrCO_3$	147·6	3·60	41·0
$PbCO_3$	267	6·47	41·3

If the crystalline forms are only approximately similar, the specific volumes also are only approximately equal, the difference being less as the angles of the two crystalline forms are more nearly equal and their axis more nearly in the same ratio. In dimorphous compounds, each modification has a density, and therefore a specific volume, peculiar to itself.

The hydrated sulphates of magnesium, zinc, nickel, cobalt, and iron, which have the general formula, $M''SO_4 + 7H_2O$ (M'' denoting a bivalent metal: see next page), and crystallise in similar forms, have specific volumes very nearly equal to 146; the double sulphates isomorphous with potassio-cupric sulphate, $K_2Cu(SO_4)_2 + 6H_2O$, have specific volumes ranging between 198 and 216; and the alums, *e.g.*, $KAl(SO_4)_2+12H_2O$ have specific volumes ranging between 276 and 281.

The specific volumes of liquid compounds have been studied chiefly with relation to organic compounds. The most general relation observed is that: *Differences of specific volume are in numerous instances proportional to the differences between the corresponding chemical formulæ.* Thus liquids whose formulæ differ by nCH_2 differ in specific volume by n times 22; for example, methyl formate $CH_3.CHO_2$, and ethyl butyrate $C_2H_5.C_4H_7O_2$, which differ by $4CH_2$, have specific volumes differing by nearly 4 × 22.

Atomicity, Quantivalence.

We have seen that the atomic weight of an element is in some cases equal to its equivalent weight, in others, twice, three times, four times, &c., as great as the equivalent weight; in other words, an atom of certain elements can replace or be substituted for only one atom of hydrogen, whereas the atoms of other elements can replace, 1, 2, 3, 4, &c., atoms of hydrogen. Thus, when sodium dissolves in hydrochloric acid, each atom of sodium replaces 1 atom of hydrogen; but when zinc dissolves in the same acid, each atom of zinc takes the place of 2 atoms of hydrogen: thus

$$\begin{aligned} Na &+ HCl = NaCl + H \\ Zn &+ 2HCl = ZnCl_2 + H_2 \end{aligned}$$

Here it is seen that an atom of zinc is equal in combining, or saturating power to 2 atoms of hydrogen. In like manner, antimony and bismuth form trichlorides, $AlCl_3$ and $BiCl_3$, in which the atom of the metal performs the same chemical function as 3 atoms of hydrogen, that is to say, it saturates 3 atoms of chlorine; so also tin in the tetrachloride is equivalent to 4H, and phosphorus in the pentachloride, PCl_5, to 5H.

This difference of equivalent, combining or saturating power, is called quantivalence or atomicity, and is sometimes denoted by placing dashes or Roman numerals to the right of the symbol of an element, and at the top, as O'', B''', C^{iv}, &c.; and the several elements are designated as—

Univalent elements, or Monads, as H
Bivalent ,, Dyads, ,, O''
Trivalent ,, Triads, ,, B'''
Quadrivalent ,, Tetrads, ,, C^{iv}
Quinquivalent ,, Pentads, ,, P^{v}
Sexvalent ,, Hexads, ,, W^{v}

Elements of even equivalency, viz., the dyads, tetrads, and hexads, are also included under the general term artiads,* and those of uneven equivalency, viz., the monads, triads, and pentads, are des nated generally as perissads.*

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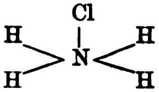
* Αρτιος, even.

Another method of indicating the equivalent values of t elementary atoms, and the manner in which they are satisfied combination, is to arrange the symbols in diagrams in which ea element is connected with others by a number of lines, or conne ing bonds corresponding with its degree of equivalence; a mon being connected with other elements by only one such bond, a tri by three, a hexad by six, &c., as in the following examples:—

Water, H_2O . . . . . . $H—O—H$

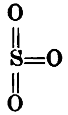
Carbon dioxide, CO_2 . . . . $O=C=O$

Ammonium chloride, NH_4Cl . .



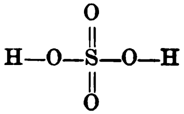
$$\begin{array}{c}H\\ H\end{array}\!\!>\overset{\overset{Cl}{|}}{N}<\!\!\begin{array}{c}H\\ H\end{array}$$

Sulphuric oxide, SO_3 . . . .



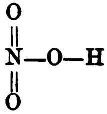
$$\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}=O$$

Sulphuric acid, H_2SO_4 . .



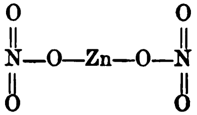
$$H—O—\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}—O—H$$

Nitric acid, HNO_3 . . . . .



$$\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{N}}—O—H$$

Zinc nitrate, ZnN_2O_6 . .



$$\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{N}}—O—Zn—O—\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{N}}$$

It must be distinctly understood that these formulæ—which a called graphic, structural, or constitutional formulæ—a not intended to represent the actual arrangement of the atoms in compound; indeed, even if we had a distinct notion of the mann in which the atoms of any compound are arranged, it could not 1 adequately represented on a plane surface. The lines connecti the different atoms indicate nothing more than the number of units of equivalency belonging to the several atoms, and the manner in which they are disposed of by combination with those of other atoms. Thus the formula for nitric acid indicates that two of the three constituent oxygen-atoms are combined with the nitrogen alone, and are consequently attached to that element by both their units of equivalency, whereas the third oxygen-atom is combined both with nitrogen and with hydrogen.*

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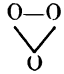
* Περισσός, uneven.

By inspection of the preceding diagrams, it will be observed that every atom of a compound has each of its units of equivalency satisfied by combination with a unit belonging to some other atom. Such, indeed, is the case in every saturated or normal compound. Accordingly, it is found that in all such compounds the sum of the perissad elements is always an even number. Thus a compound may contain two, four, six, &c., monad atoms, as ClH, OH_2, CH_4, C_2H_6, C_3H_8, SiH_3Cl; or one monad and one triad atom, as BCl_3; or one pentad and five monads, as NH_4Cl; but never an uneven number of perissad atoms. This is the "law of even numbers," announced some years ago by Gerhardt and Laurent as a result of observation. It was long received with doubt, but has now been confirmed by the analysis of so many well-defined compounds, that a departure from it is looked upon as a sure indication of incorrect analysis.

For a similar reason, the atoms of elementary bodies rarely exist in the free state, but, when separated from any compound, tend to combine with other atoms, either of the same or of some other element. Perissad elements, like hydrogen, chlorine, nitrogen &c., separate from their compounds in pairs; their molecule contains two atoms, *e.g.*, H—H. Artiad elements may unite in groups of two, three, or more; thus the molecule of oxygen, in its ordinary state, probably contains two atoms, that of ozone three atoms; thus—

Oxygen, ... $O=O$

Ozone, ...



The tendency of elementary atoms to separate in groups is shown in various ways. Thus when copper hydride, Cu_2H_2 (to be hereafter described), is decomposed by hydrochloric acid, a quantity of hydrogen is given off equal to twice that which is contained in the hydride itself; thus—

---

* For lecture and class illustration, solid diagrams are constructed, with wooden balls of various colours, to represent the atoms, having holes for the insertion of connecting rods; these representations are called *glyptic formulæ*. Objection is sometimes made to the use of such illustrations, on the ground that they might lead the pupils to imagine that the atoms forming a molecule are actually connected together by material bonds. As well might objection be taken to the use of an artificial globe in teaching geography and astronomy, lest the student should acquire curious notions about the *brazen* meridian and *the wooden* horizon.

$$Cu_2H_2 + 2HCl = Cu_2Cl_2 + 2HH.$$

This action is precisely analogous to that of hydrochloric acid on cuprous oxide:

$$Cu_2O + 2HCl = Cu_2Cl_2 + H_2O.$$

In the latter case, the hydrogen separated from the hydrochloric acid unites with oxygen, in the former with hydrogen. Again, when solutions of sulphurous acid and sulphydric acid are mixed, the whole of the sulphur is precipitated:

$$H_2SO_3 + 2H_2S = 3H_2O + S.S_2,$$

the action being similar to that of sulphurous acid on selenhydric acid:

$$H_2SO_3 + 2H_2Se = 3H_2O + S.Se_2.$$

In the one case, a sulphide of selenium is precipitated; in the other a sulphide of sulphur. The precipitation of iodine, which takes place on mixing hydriodic acid with iodic acid, affords a similar instance of the combination of homogeneous atoms:

$$\underset{\text{Hydriodic acid.}}{5HI} + \underset{\text{Iodic acid.}}{HIO_3} = \underset{\text{Water.}}{3H_2O} + \underset{\text{Free iodine.}}{3II}$$

Another striking illustration of this mode of action is afforded by the reduction of certain metallic oxides by hydrogen dioxide. When silver oxide is thrown into this liquid, water is formed, the silver is reduced to the metallic state, and a quantity of oxygen is evolved equal to twice that which is contained in the silver oxide:

$$Ag_2O + H_2O_2 = H_2O + Ag_2 + OO.$$

Further, elementary bodies frequently act upon others as if their atoms were associated in binary groups. Thus chlorine acting upon potassium oxide forms two compounds, the chloride and hypochlorite of potassium (p. 193):

$$ClCl + KKO = KCl + KClO.$$

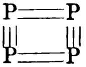
Again, in the action of chlorine upon many organic compounds, one atom of chlorine removes one atom of hydrogen as hydrochloric acid, while another atom of chlorine takes the place of the hydrogen thus removed. For example, in the formation of chloracetic acid by the action of chlorine on acetic acid:

$$\underset{\text{Acetic acid}}{C_2H_4O_2} + ClCl = HCl + \underset{\text{Chloracetic acid.}}{C_2H_3ClO_2}$$

Similarly, when metallic sulphides oxidise in the air, both the metal and the sulphur combine with oxygen; and sulphur acting upon potash forms both a sulphide and a thiosulphate. In all these cases the atoms of the elementary bodies act in pairs.

On the supposition that the molecules of elementary bodies in the gaseous state are made up of two atoms, the specific volumes of these gases will come under the same law as that which applies to compounds (p. 253): and it may then be stated generally, that, with the few exceptions already noticed, *the specific gravities of all bodies, simple and compound, in the gaseous state, are equal to half their molecular weights;* or the *specific volumes* (the quotients of the molecular weights by the specific gravities) *are equal to* 2.

There are, however, two elements, namely, phosphorus and arsenic, which at all temperatures hitherto attained exhibit a vapour-density twice as great as that which they should have according to the general law, that of phosphorus being always 62, and that of arsenic 150. This has been explained by supposing that the molecule of each of these two elements in the free state contains four atoms instead of two, as is the case with most elementary bodies; thus the molecule of phosphorus is supposed to be represented by the formula,

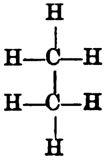


Variation of Equivalency.—Multivalent elements often exhibit varying degrees of equivalency. Thus carbon, which is quadrivalent in marsh gas, CH_4, and in carbon dioxide, CO_2, is only bivalent in carbon monoxide, CO; nitrogen, which is quinquivalent in sal-ammoniac, NH_4Cl, and the other ammonium salts, and in nitrogen pentoxide, N_2O_5, is trivalent in ammonia, NH_3, and in nitrogen trioxide, N_2O_3, and univalent in nitrogen monoxide N_2O; sulphur, also, which is sexvalent in sulphur trioxide, SO_3, is quadrivalent in sulphur dioxide, SO_2, and bivalent in hydrogen sulphide, H_2S, and in many metallic sulphides. In these cases, and in others of varying equivalency, the variation mostly takes place by two units of equivalency. It is not very easy to account for these variations; but it is observed in all cases that the compounds in which the equivalency of a polygenic element is most completely satisfied are more stable than the others, and that the latter tend to pass into the former by taking up the required number of univalent or bivalent atoms; thus, carbon monoxide, CO, easily takes up another atom of oxygen to form the dioxide, CO_2; nitrogen trioxide, N_2O_3, is readily converted into the pentoxide, N_2O_5; ammonia, NH_3, unites readily with hydrochloric acid to form sal-ammoniac, NH_4Cl, &c. Similar phenomena are exhibited by many organo-metallic bodies, as will be explained further on.

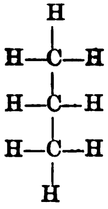
From this it seems most probable that the true quantivalence or atomicity of a polygenic element is that which corresponds with the maximum number of monad atoms with which it can combine, but that one or two pairs of its units of equivalency may, under certain circumstances, remain unsaturated. Whether a saturated or an unsaturated compound is formed, will depend on a variety of conditions, often in great measure on the relative quantities of the acting substances. Thus phosphorus, which is a pentad element, forms with chlorine either a trichloride, PCl_3, or a pentachloride, PCl_5, according as the phosphorus or the chlorine is in excess (p. 240).*

In compounds containing two or more atoms of the same multivalent element, one or more units of equivalence belonging to each of these atoms may be neutralised by combination with those of another atom of the same kind, so that the element in question will appear to enter into the compound with less than its normal degree of equivalence. Thus in ethane, or dimethyl, C_2H_6, which is a perfectly stable compound, having no tendency to take up an additional number of atoms of hydrogen or any other element, the carbon appears to be trivalent instead of quadrivalent; similarly in propane, C_3H_8, its equivalence appears to be reduced to $\frac{8}{3}$; and in quartane or diethyl, C_4H_{10}, to $\frac{5}{2}$. In all these cases, however, the diminution of equivalent value in the carbon atoms is only apparent, as may be seen from the following formulæ:

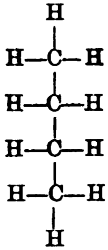
Ethane.



Propane.



Quartane.



or, more shortly, omitting the equivalent marks of the monad atoms:

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* See also Erlenmeyer, Lehrbuch der organischen Chemie, p. 41.

$$\begin{array}{ccc}
\textbf{Ethane.} & \textbf{Propane.} & \textbf{Quartane.} \\
\begin{array}{c} CH_3 \\ | \\ CH_3 \end{array} &
\begin{array}{c} CH_3 \\ | \\ CH_2 \\ | \\ CH_3 \end{array} &
\begin{array}{c} CH_3 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CH_3 \end{array}
\end{array}$$

In each of these compounds, every carbon atom, except the two outside ones, has two of its units of equivalence satisfied by combination with those of the neighbouring carbon atoms, while each of the two exterior ones has only one unit thus satisfied. Hence, in any similarly constituted compound containing n carbon atoms, the number of units of equivalence remaining to be satisfied by the hydrogen atoms is $4n-2(n-2)-2=2n+2$. The general formula of this series of hydrocarbons is, therefore, C_nH2n+2, and the equivalent value of the carbon is $\frac{2n+2}{n}$.

In other cases, multivalent atoms may be united by two or more of their units of equivalence, so that their combining power may appear to be still further reduced, as in the hydrocarbon, C_2H_4, in which the carbon may be apparently bivalent, and in C_2H_2, in which it may appear to be univalent; thus—

$$\begin{array}{ccc}
\begin{array}{c} H—C—H \\ \| \\ H—C—H \end{array} & \qquad &
\begin{array}{c} C—H \\ ||| \\ C—H\,. \end{array}
\end{array}$$

In most cases, the equivalent value or atomicity of an element is most safely determined by the number of monad atoms with which it can combine. Of dyad atoms, indeed, any element or compound may take up an indefinite number, without alteration of its quantivalence or combining power: for each dyad atom, possessing two units of equivalency, neutralises one unit in the compound which it enters, and introduces another, leaving, therefore, the combining power of the compound just what it was before. Thus potassium forms only one chloride, KCl, and is therefore univalent or monadic; but in addition to the oxide, K_2O, corresponding with this chloride, it likewise forms two others, viz., K_2O_2 and K_2O_4, in the former of which it might be regarded as dyadic, and in the latter as tetradic; but the manner in which dyad oxygen enters these compounds is easily seen by inspection of the following diagrams:—

$$\begin{array}{ccc}
\textbf{Monoxide.} & \textbf{Dioxide.} & \textbf{Tetroxide.} \\
O\begin{array}{l} <K \\ \phantom{<}K \end{array} &
\begin{array}{c} O—K \\ | \\ O—K \end{array} &
\begin{array}{c} O—K \\ | \\ O \\ | \\ O \\ | \\ O—K\,. \end{array}
\end{array}$$

It is evident that any number of oxygen-atoms might, in like manner, be inserted without disturbing the balance of equivalency. If, indeed, we turn to the sulphides of potassium, in which the sulphur is dyadic, like oxygen, we find the series, K_2S, K_2S_2, K_2S_3, K_2S_4, K_2S_5, the constitution of which may be represented in a precisely similar manner. Hence the quantivalence of any element is, for the most part, best determined by the composition of its chlorides, bromides, iodides, or fluorides, rather than by that of its oxides or sulphides. In some cases, however, as will be seen further on, the combinations of an element with oxygen afford the best means of determining its quantivalence or combining capacity.

Compound Radicles.—Suppose one or more of the component atoms of a fully saturated molecule to be removed: it is clear that the remaining atom or group of atoms will no longer be saturated, but will have a combining power corresponding with the number of units of equivalency removed. Such unsaturated groups are called residues or radicles. Methane, CH_4, is a fully saturated compound; but if one of its hydrogen atoms be removed, the residue CH_3 (called methyl), will be ready to combine with one atom of a univalent element, such as chlorine, bromine, &c., forming the compounds CH_3Cl, CH_3Br, &c.; two atoms of it unite in like manner with one atom of oxygen, sulphur, and other bivalent elements, forming the compounds $O''(CH_3)_3$, $S''(CH_3)_2$, &c.; three atoms with nitrogen yielding $N'''(CH_3)_3$, &c.

The removal of two hydrogen-atoms from CH_4 leaves the bivalent radicle CH_2, called methene, which yields the compounds CH_2Cl_2, CH_2O, CH_2S, &c. The removal of three hydrogen atoms from CH_4 leaves the trivalent radicle CH, which, in combination with three chlorine-atoms, constitutes chloroform, $CHCl_3$. And, finally, the removal of all four hydrogen-atoms from CH_4 leaves the quadrivalent radicle carbon, C^{iv}, capable of forming the compounds CCl_4, CS_2, &c.

In like manner, *ammonia*, NH_3, in which the nitrogen is trivalent, yields, by removal of one hydrogen-atom, the univalent radicle amidogen, NH_2, which with one atom of potassium forms potassamine, NH_2K, and when combined with one atom of the univalent radicle methyl, CH_3, forms methylamine, $NH_2(CH_3)$, &c. The abstraction of two hydrogen-atoms from the molecule NH_3, leaves the bivalent radicle imidogen, NH, which with two methyl-atoms forms dimethylamine, $NH(CH_3)_2$, &c.; and the removal of all three hydrogen-atoms from NH_3, leaves nitrogen itself, which frequently acts a trivalent element or radicle, forming tripotassamine, NK_3, trimethylamine, $N(CH_3)_3$, &c.

Finally, the molecule of *water*, OH_2, by losing an atom of hydrogen, is converted into the univalent radicle hydroxyl, OH, which, in its relations to other bodies, is analogous to chlorine, bromine, and iodine, and may be substituted in combination for one atom of hydrogen or other monads. Thus, water itself may be regarded as

H.OH, analogous to hydrochloric acid, HCl; potassium hydroxide as K.OH, analogous to potassium chloride; barium hydroxide, as $Ba''.(OH)_2$, analogous to barium chloride, $Ba''Cl_2$.

In a similar manner, the univalent radicle, potassoxyl, KO, may be derived from potassium hydroxide; the bivalent radicle, zincoxyl, ZnO_2, by abstraction of H_2 from zinc hydroxide, $Zn''H_2O_2$. The essential character of these oxygenated radicles is that each of the oxygen-atoms contained in them is united to the other atoms by one unit of equivalency only, so that the radicle has necessarily one or two units unconnected; thus—

Hydroxyl, ...	H—O—
Potassoxyl, ...	K—O—
Zincoxyl, . . .	—O—Zn—O—

From the preceding explanations of the mode of derivation of compound radicles, it is clear that there is no limit to the number of them which may be supposed to exist; in fact, it is only necessary to suppose a number of units of equivalency abstracted from any saturated molecule, in order to obtain a radicle of corresponding combining power or equivalent value. But unless a radicle can be supposed to enter into a considerable number of compounds, thus forming them into a group, like the salts of the same metal, there is nothing gained in point of simplicity or comprehensiveness by assuming its existence.

It must also be distinctly understood that these compound radicles do not necessarily exist in the separate state, and that those of uneven equivalency, like methyl, cannot exist in that state, their molecules, if liberated from combination with others, always doubling themselves, as we have seen to be the case with most of the elementary bodies. Thus hydroxyl —O—H is not known in the free state, the actually existing compound containing the same proportions of hydrogen and oxygen being O_2H_2 or H—O—O—H. In like manner methyl, CH_3, has no separate existence, but dimethyl, C_2H_6, is a known compound:—

Methyl. Dimethyl.

$$\begin{array}{c} CH_3 \\ | \end{array} \qquad\qquad \begin{array}{c} CH_3 \\ | \\ CH_3 \end{array}$$

Relations between Atomic Weight and Quantivalence.—A very remarkable relation has been shown to exist between the quantivalence of the elements and the numerical order of their atomic weights. Arranging the elements in vertical columns according to this order, as in the following table, we find that, with the exception of certain metals belonging to the iron and platinum groups, they all arrange themelves in such a manner, that the first horizontal line is occupied by the monad elements, the second by the dyads, the third by the triads, &c., as indicated by the composition of the chlorides in the last column of the table, where R denotes a metal or hydrogen. Hydrogen itself stands alone, there being no known element intermediate between it and the monad metal lithium. This relation of the elementary bodies, which is called the "periodic law," was first pointed out by Newlands in 1864, and afterwards developed by Odling and Mendelejeff.

Arrangement of Elements in the order of their Atomic Weights.

H 1	Li 7	Na 23	K 39	Cu 63	Rb 85	Ag 108	Cs 133	...	Au 199	...	RCl
	Be 9·4	Mg 24	Ca 40	Zn 65	Sr 87	Cd 112	Ba 137	...	Hg 200	...	RCl_2
	B 11	Al 27	...	Ga 68	Y 88	In 113	Di 138	Eb 178	Tl 204	...	RCl_3
	C 12	Si 28	Ti 48	...	Zr 90	Sn 118	Ce 140	La 180	Pb 207	Th 231	RCl_4
	N 14	P 31	V 51	As 75	Nb 94	Sb 122	...	Ta 182	Bi 210	...	RCl_5
	O 16	S 32	Cr 52	Si 78	Mo 96	Te 125?	...	W 184	...	U 240	RCl_6
	F 19	Cl 35·5	Mn 55	Br 80	...	I 127	...	...	...	...	RCl_7
			Fe 56	...	Ru 104	...	...	Os 195			
			Co 59	...	Rh 104	...	...	Ir 197			
			Ni 59	...	Pd 106	...	...	Pt 198			
			Cu 63	...	...	...	...	...			

Of the elements in the first row, lithium, sodium, potassium, rubidium, silver, and cæsium are shown to be monadic or univalent, by their combinations with chlorine and oxygen, *e.g.*, NaCl and $\begin{matrix}Na\\Na\end{matrix}>O$. Copper may be regarded as univalent in one series of its compounds, viz., the cuprous compounds, as in the chloride CuCl and the oxide Cu_2O, though in its most stable compounds it is bivalent, and appears to be more nearly related to the metals of the iron group. The place of gold in the series is somewhat exceptional, since, though univalent in the aurous compounds, as AuCl, it is trivalent in the more stable auric compounds, as $AuCl_3$.

The elements in the second row are all dyads, with the exception perhaps of beryllium, which has some analogies to the triads.

Of the elements in the third row, boron, gallium, indium, and thallium are undoubtedly triads. Aluminium forms a trichloride. $AlCl_3$, and a corresponding oxide, Al_2O_3, also a volatile methyl-compound, $Al(CH_3)_3$, the vapour-density of which indicates that the molecule, as represented by this formula, has the normal 2-volume condensation (p. 253). It is true that the chloride, which is also volatile, exhibits a vapour-density agreeing rather with the doubled formula, Al_2Cl_6, which would indicate that aluminium is a tetrad, the chloride having the constitution $\begin{matrix}AlCl_3\\|\\AlCl_3\end{matrix}$; but this chloride boils at a very high temperature, and it is therefore probable that the temperature at which its vapour-density was actually taken was not sufficiently raised above the boiling point to bring the compound into the state of a perfect gas (p. 253).

Yttrium, didymium, and erbium are usually regarded as dyads; indeed their atomic weights, as determined by experiment, are not those given in the preceding table. Mendelejeff, however, from certain considerations which will be noticed hereafter, proposes to regard them as triads, and to alter their atomic weights accordingly. The matter is for the present altogether doubtful, though perhaps on the whole the balance of argument is against Mendelejeff's suggestion.

The elements in the fourth row are undoubtedly tetradic, with the exception of lanthanum, which is more generally regarded as a dyad.

Of the elements in the fifth row, phosphorus, antimony, niobium, and tantalum form pentachlorides. Nitrogen is quinquivalent in the ammonium-compounds, as in the chloride NH_4Cl. Vanadium, arsenic, and bismuth do not combine with more than 3 atoms of chlorine, bromine, or iodine; but bismuth forms an oxychloride, $BiOCl_3$ or $O{=}BiCl_3$, in which it is quinquivalent, and vanadium forms the analogous compound, $VOCl_3$. Arsenic does not form a similar oxychloride; but its highest oxide, As_2O_5, is the exact analogue of phosphoric oxide, P_2O_5, and vanadic oxide, V_2O_5, and forms a series of salts, the arsenates, which are isomorphous with the phosphates and vanadates. For these reasons arsenic is likewise regarded as a pentad.

Among the elements in the sixth row, chromium forms a hexfluoride and tungsten a hexchloride; uranium forms an oxychloride, UO_2Cl_2, and a trioxide, UO_3. Sulphur, selenium, and tellurium, so far as regards their hydrogen-compounds, H_2S, &c., are dyads; but with regard to their combinations with chlorine, they are tetrads, and sulphur is known to form certain organic compounds in which it is tetradic, and others in which it is hexadic.* Moreover the chemical relations of the sulphates are much more clearly represented by formulæ in which sulphur is supposed to be hexadic, like that given for sulphuric acid on p. 257, than by formulæ into which it enters as a dyad, such as, $H{-}O{-}O{-}S{-}O{-}O{-}H$, inasmuch as compounds in which dyadic elements are linked together in one row, are for the most part very unstable, like the higher oxides and sulphides of potassium (pp. 262, 263). These three elements are therefore best regarded as hexads, though they sometimes enter into combination as tetrads, and very frequently as dyads.

Oxygen, in its combinations with hydrogen, and with most of the metals, undoubtedly acts as a dyad; but it appears also to be capable of higher degrees of combination; with silver, for example, it forms the two oxides, Ag_2O and Ag_4O, in the latter of which it is tetradic; and from its close analogies to sulphur, and the place of its atomic weight in the series, it may be classed with the hexads.

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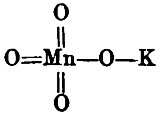
* Sulphur triethiodide, $S^{iv}\left\{\begin{matrix}(C_2H_5)_3\\ I\end{matrix}\right.$

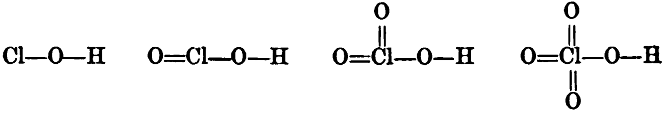
Sulphur diethene-dibromide $S^{vi}\left\{\begin{matrix}(C_2H_4)''\\ (C_2H_4)''\\ Br_2\end{matrix}\right.$

Of the elements in the seventh row, manganese appears to form a heptachloride, $MnCl_7$, though the composition of this chloride has not perhaps been very distinctly made out; but in the permanganates the metal appears to be decidedly heptadic; the potassium salt, $KMnO_4$, for example, may be represented by the structural formula:



$$O{=}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{Mn}}{-}O{-}K$$

The perchlorates, *e.g.* $KClO_4$, are similar to the permanganates in composition and in crystalline form, and may therefore be supposed to have a similar constitution, the chlorine in them being septivalent; in fact, the four oxy-acids of chlorine form a regular series in which the quantivalence of the chlorine varies by two units from 1 to 7; thus—



$$Cl{-}O{-}H \qquad O{=}Cl{-}O{-}H \qquad O{=}\overset{\overset{\displaystyle O}{\|}}{Cl}{-}O{-}H \qquad O{=}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{Cl}}{-}O{-}H$$

Hypochlorous. Chlorous. Chloric. Perchloric.

Iodic acid, IO_3H, and periodic acid, IO_4H, are exactly similar in constitution to chloric and perchloric acids, and the corresponding oxides or anhydrides I_2O_5, I_2O_7 are likewise known (p. 200): hence iodine also may be regarded as a heptad. Bromic acid, BrO_3H, is similar to chloric acid, but perbromic acid has not yet been obtained; and of fluorine no oxygen-compound is known; but from the close analogy in the reactions of these four elements, Cl, Br, I, and F, and the manner in which they replace one another in combination, there can be no doubt that they belong to the same group. In their combinations with hydrogen, and in the reactions in which they replace hydrogen and one another in combination, they invariably act as monads, the substitution taking place atom for atom.

Lastly, with regard to the elements (all metallic) which cannot be included in either of the seven horizontal series above considered. The atomic weights of three of these metals, viz., iron, cobalt, and nickel, have values between those of manganese and copper; and of the other six, called platinum metals, three, viz., ruthenium, rhodium, and palladium, have atomic weights intermediate between those of molybdenum (96) and silver (108); and the other three, viz., osmium, iridium, and platinum, are in like manner intermediate between tungsten (184) and gold (199).

These intermediate elements, Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt, constitute a group of themselves (the eighth), some of the members of which, viz., Ru and Os, form tetroxides (analogous to octochlorides), and may therefore be regarded as octads. None of them, however, form chlorides containing more than 4 atoms of chlorine to one atom of metal.

The blank spaces in the preceding table indicate the places of elements which probably exist, but have not yet been actually discovered. An anticipated discovery of this kind has, however, been actually realised. When the table was drawn up, a blank in the place now occupied by gallium indicated the probable existence of a trivalent element intermediate in atomic weight between zinc and arsenic. This element was provisionally designated *ekaluminium* by Mendelejeff, who predicted, from its position in the series, what its chief properties ought to be. The discovery of gallium, with the atomic weight 68, has verified this prediction.

CRYSTALLISATION; CRYSTALLINE FORM.

Almost every substance, simple or compound, capable of existing in the solid state, assumes, under favourable circumstances, a distinct geometrical figure, usually bounded by plane surfaces, and having angles of constant value. The faculty of crystallisation seems to be denied only to a few bodies, chiefly highly complex organic principles, which stand, as it were, upon the very verge of organisation, and which, when in the solid state, are frequently characterised by a kind of beady or globular appearance, well known to microscopical observers.

The most beautiful examples of crystallisation are to be found among natural minerals, the results of exceedingly slow changes constantly occurring within the earth. It is invariably found that artificial crystals of salts, and other soluble substances which have been slowly and quietly deposited, surpass in size and regularity those of more rapid formation.

Solution in water or some other liquid is a very frequent method of effecting crystallisation. If the substance be more soluble at a high than at a low temperature, then a hot and saturated solution left to cool slowly will generally be found to furnish crystals: this is a very common case with salts and various organic principles. If it be equally soluble, or nearly so, at all temperatures, then slow spontaneous evaporation in the air, or over a surface of oil of vitriol, often proves very effective.

Fusion and slow cooling may be employed in many cases: that of sulphur is a good example: the metals, when thus treated, usually afford traces of crystalline figure, which sometimes become very beautiful and distinct, as with bismuth. A third condition under which crystals very often form is in passing from the gaseous to the solid state, of which iodine affords a good instance. When by any of these means time is allowed for the symmetrical arrangement of the particles of matter at the moment of solidification, crystals are produced.

That crystals owe their figure to a certain regularity of internal structure is shown both by their mode of formation and also by the peculiarities attending their fracture. A crystal placed in a slowly evaporating saturated solution of the same substance, grows or increases by a continued deposition of fresh matter upon its sides, in such a manner that the angles formed by the meeting of the latter remain unaltered.

The tendency of most crystals to split in particular directions, called by mineralogists *cleavage*, is a certain indication of regular structure, while the optical properties of many among them, and their mode of expansion by heat, point to the same conclusion.

It may be laid down as a general rule that every substance has its own crystalline form, by which it may very frequently be recognised at once—not that each substance has a different figure, although very great diversity in this respect is to be found. Some forms are much more common than others, as the cube and six-sided prism, which are very frequently assumed by a number of bodies not in any way related.

The same substance may assume, under different sets of circumstances, as at high and low temperatures, two different crystalline forms, in which case it is said to be *dimorphous*. Sulphur and carbon furnish, as already noticed, examples of this curious fact; another case is presented by calcium carbonate in the two modifications of calc spar and arragonite, both chemically the same, but physically different. A fourth example might be given in mercuric iodide, which also has two distinct forms, and even two distinct colours, offering as great a contrast as those of diamond and graphite.

Crystallographic Systems.—When a crystal of simple form is attentively considered, it becomes evident that certain directions can be pointed out in which straight lines may be imagined to be drawn, passing through the central point of the crystal from side to side, from end to end, or from one angle to that opposed to it, &c., about which lines the particles of matter composing the crystal may be conceived to be symmetrically built up. Such lines, or *axes*, are not always purely imaginary, however, as may be inferred from the remarkable optical properties of many crystals: upon their number, relative lengths, position, and inclination to each other, depends the outward figure of the crystal itself.

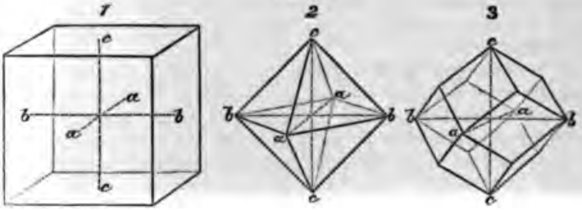
All crystalline forms may upon this plan be arranged in six classes or systems; these are the following.

1. **The monometric, regular, or cubic system** (fig. 125).—The crystals of this division have three equal axes, all placed at right angles to each other. The most important forms are the *cube* (1), *the regular octohedron* (2), and the *rhombic dodecahedron* (3).

The letters *a—a*, *b—b*, *c—c* (fig. 125), show the termination of the three axes, placed as stated.

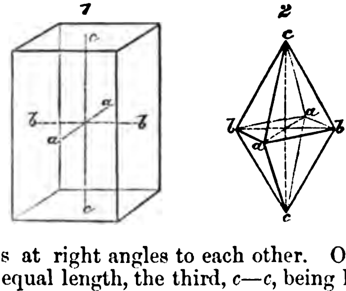
Very many substances, both simple and compound, assume these forms, as most of the metals, carbon in the state of diamond, common salt, potassium iodide, the alums, fluor-spar, iron bisulphide, garnet, spinelle, &c.

Fig. 125.



2. **The dimetric, quadratic, square prismatic, or pyramidal system.**—The crystals of this system (fig. 126) are also symmetrical about three axes at right angles to each other. Of these, however, two only are of equal length, the third, *c—c*, being longer or shorter. The most important forms are, the *right square prism* (1), and the *right square-based octohedron* (2).

Fig. 126.



Examples of these forms are to be found in zircon, native stannic oxide, apophyllite, yellow potassium ferrocyanide, &c.

3. **The rhombohedral system** (fig. 127.)—This is very important and extensive; it may be characterised by *four* axes,[*] three of which are equal, in the same plane, and inclined to each other at angles

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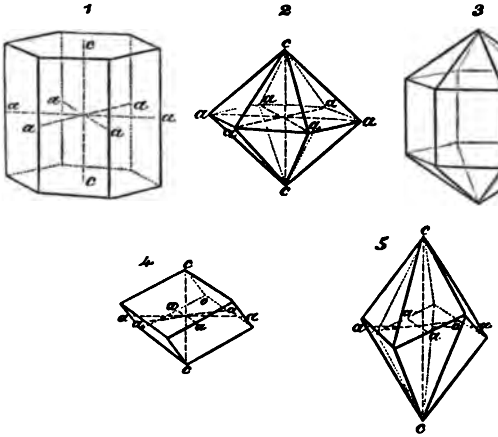
[*] This reference to *four* axes is a mere matter of convenience; *three* axes are sufficient for the determination of any solid figure whatever.

of 60°, while the fourth or principal axis is perpendicular to them all. The principal forms are,—the *regular six-sided prism* (1), the *regular double six-sided pyramid* (2), the *rhombohedron* (4), and the *scalenohedron* (5), a figure bounded by twelve scalene triangles.

Examples are found in ice, calcspar, sodium nitrate, beryl, quartz or rock-crystal, and the semi-metals, arsenic, antimony, and tellurium.

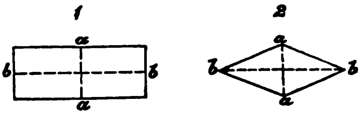
A combination of the regular six-sided prism and double six-sided pyramid (3) is a common form of quartz.

Fig. 127.



4. **The trimetric, rhombic, or right prismatic system.**—This is characterised by three axes of unequal lengths, placed at right angles to each other, as in the *right rectangular prism*, the *right rhombic prism*, the *right rectangular-based octohedron*, and the *right rhombic-based octohedron.*

Fig. 128.



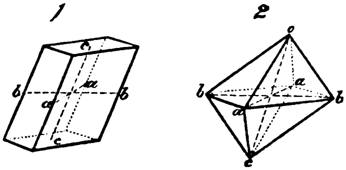
The bases of these forms are represented in fig. 128, (1) and (2). Let the reader imagine a straight line passing through the centre of each of these figures, perpendicular to the plane of the paper; this will represent the vertical axis. The octohedrons will be formed by joining the ends of this vertical line with the angles of the bases, and the prisms by vertical planes passing through the sides of the base, and terminated by horizontal planes passing through the extremities of the vertical axis. The perspective forms of these trimetric prisms and octohedrons are similar to those of the dimetric system (fig. 126).

The system is exemplified in sulphur crystallised at a low temperature, arsenical iron pyrites, potassium nitrate and sulphate, barium sulphate, &c.

5. **The monoclinic or oblique prismatic system.**—Crystals belonging to this group have also three axes, which may be all unequal; two of these (the secondary) are placed at right angles, the third being so inclined as to be oblique to one and perpendicular to the other. To this system may be referred the four following forms:—*The oblique rectangular prism*, the *oblique rhombic prism*, the *oblique rectangular-based octohedron*, the *oblique rhombic-based octohedron*.

The bases of these monoclinic forms are identical in form with those of the trimetric system, fig. 128, (1) and (2). The principal axis may be represented by a line passing through the plane of the paper at the middle point, perpendicular to *a a*, and oblique to *b b*. The perspective forms are shown in fig. 129.

Fig. 129.



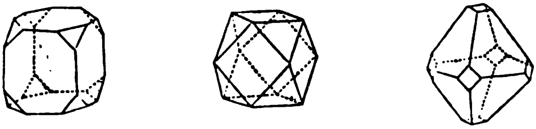
Such forms are taken by sulphur crystallised by fusion and cooling, by realgar, sulphate, carbonate and phosphate of sodium, borax, green vitriol, and many other salts.

6. **The triclinic, anorthic, or doubly oblique prismatic system.**—The crystalline forms comprehended in this division are, from their great apparent irregularity, exceedingly difficult to study and understand. In them are traced three axes, which may be all unequal in length, and are all oblique to each other, as in the *doubly-oblique prism*, and in the *doubly-oblique octohedron*. The perspective forms are similar to those of the monoclinic system.

Copper sulphate, bismuth nitrate, and potassium quadroxalate afford illustrations of these forms.

Primary and Secondary Forms.—If a crystal increase in magnitude by equal additions on every part, it is quite clear that its figure must remain unaltered; but if, from some cause, this increase should be partial, the newly deposited matter being distributed unequally, but still in obedience to certain definite laws, then alterations of form are produced, giving rise to figures which have a direct geometrical connection with that from which they are derived. If, for example, in the cube, a regular omission of successive rows of particles of matter in a certain order be made at each solid angle, while the crystal continues to increase elsewhere, the result will be the production of small triangular planes, which, as the process advances, gradually usurp the whole of the surface of the crystal, and convert the cube into an octohedron. The new planes are called *secondary*, and their production is said to take place by regular *decrements* upon the solid angles. The same thing may happen on the edges of the cube; a new figure, the rhombic dodecahedron, is then generated. The modifications which can thus be produced of the original or *primary* figure (all of which are subject to exact geometrical laws) are very numerous. Several distinct modifications may be present at the same time, and thus render the form exceedingly complex.

Fig. 130.

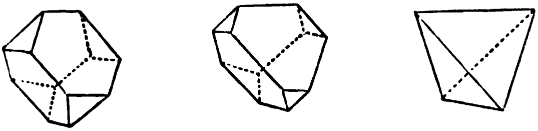


Passage of cube to octohedron.

Crystals often cleave parallel to all the planes of the primary figure, as in calcspar, which offers a good illustration of this perfect cleavage. Sometimes one or two of these planes have a kind of preference over the rest in this respect, the crystal splitting readily in these directions only.

A very curious modification of the figure sometimes occurs by the excessive growth of each alternate plane of the crystal; the rest become at length obliterated, and the crystal assumes the character called *hemihedral* or *half-sided*. This is well seen in the production of the tetrahedron from the regular octohedron (fig. 131.

Fig. 131.



Passage of octohedron to tetrahedron.

and of the rhombohedric form by a similar change from the double six-sided pyramid (fig. 127, 2).

Forms belonging to the same crystallographic system are related to each other by several natural affinities.

1. *It is only the simple forms of the same system that can combine into a complex form.*—For in all fully developed (holohedral) natural crystals, it is found that all the similar parts, if modified at all, are modified in an exactly similar manner (in hemihedral forms, half the similar edges and angles alternately situated are similarly modified). Now this can be the case only when the dominant form and the modifying form are developed according to the same law of symmetry. Thus, if a cube and a regular octohedron are developed round the same system of axes, each summit of the cube is cut off to the same extent by a face of the octohedron, or *vice versâ*. But a cube could never combine in this manner with a rhombic octohedron, because it would be impossible to place the two forms in such a manner that similar parts of the one should throughout replace similar parts of the other.

The crystals of each system are thus subject to a peculiar and distinct set of modifications, the observation of which very frequently constitutes an excellent guide to the discovery of the primary form itself.

2. *Crystals belonging to the same system are intimately related in their optical properties.*—Crystals belonging to the regular system (as the diamond, alum, rock-salt, &c.) refract light in the same manner as uncrystallised bodies; that is to say, they have but one refractive index, and a ray of light passing through them in any direction is refracted singly. But all other crystals refract doubly, that is to say, a ray of light passing through them (except in certain directions) is split into two rays, the one called the *ordinary* ray, being refracted as it would be by an amorphous body, the other, called the *extraordinary* ray, being refracted according to peculiar and more complex laws (see LIGHT). Now, the crystals of the dimetric and hexagonal systems resemble each other in this respect, that in all of them there is one direction, called the optic axis, or axis of double refraction (coinciding with the principal crystallographic axis), along which a ray of light is refracted singly, while in all other directions it is refracted doubly; whereas in crystals belonging to the other systems, viz., the trimetric and the two oblique systems, there are always *two* directions or axes, along which a ray is singly refracted.

3. *Crystals belonging to the same system resemble each other in their mode of conducting heat.*—Amorphous bodies and crystals of the regular system conduct heat equally in all directions, so that, supposing a centre of heat to exist within such a body, the isothermal surfaces will be spheres. But crystals of the dimetric and hexagonal systems conduct equally only in directions perpendicular to the principal axis, so that in such crystals the isothermal surfaces are

ellipsoïds of revolution round that axis; and crystals belonging to either of the three other systems conduct unequally in all directions, so that in them the isothermal surfaces are ellipsoïds with three unequal axes.

Relations of Form and Constitution; Isomorphism.

Certain substances, to which a similar chemical constitution is ascribed, possess the remarkable property of exactly replacing each other in crystallised compounds, without alteration of the characteristic geometrical figure. Such bodies are said to be *isomorphous.**

For example, magnesia, zinc oxide, cupric oxide, ferrous oxide, and nickel oxide, are allied by isomorphic relations of the most intimate nature. The salts formed by these substances with the same acid and similar proportions of water of crystallisation, are identical in their form, and, when of the same colour, cannot be distinguished by the eye: the sulphates of magnesium and zinc may be thus confounded. These sulphates, too, all combine with potassium sulphate and ammonia sulphate, giving rise to double salts, whose figure is the same, but quite different from that of the simple sulphates. Indeed this connection between identity of form and parallelism of constitution runs through all their combinations.

In the same manner alumina and iron sesquioxide replace each other continually without change of crystalline figure: the same remark may be made of the oxides of potassium, sodium, and ammonium. The alumina in common alum may be replaced by iron sesquioxide, the potash by ammonia or by soda, and still the figure of the crystal remains unchanged. These replacements may be partial only: we may have an alum containing both potash and ammonia, or alumina and chromium sesquioxide. By artificial management—namely, by transferring the crystal successively to different solutions—we may have these isomorphous and mutually replacing compounds distributed in different layers upon the same crystal.

For these reasons mixtures of isomorphous salts can never be separated by crystallisation, unless their difference of solubility is very great. A mixed solution of ferrous sulphate and nickel sulphate, isomorphous salts, yields on evaporation crystals containing both iron and nickel. But if before evaporation the ferrous salt be converted into ferric salt, by chlorine or other means, then the crystals obtained are free from iron, except that of the mother-liquor which wets them. The ferric salt is no longer isomorphous with the nickel salt, and easily separates from the latter.

Absolute identity of value in the angles of crystals is not always exhibited by isomorphous substances. In other words, small variations often occur in the magnitude of the angles of crystals of compounds which in all other respects show the closest isomorphic relations. This should occasion no surprise, as there are reasons why such variations might be expected, the chief perhaps being the unequal effects of expansion by heat, by which the angles of the same crystal are changed by alteration of temperature. A good example is found in the case of the carbonates of calcium, magnesium, manganese, iron, and zinc, which are found native crystallised in the form of obtuse rhombohedrons (fig. 127, 4), not distinguishable from each other by the eye, but exhibiting small differences in their angles when accurately measured. These compounds are isomorphous, and the measurements of the obtuse angles of their rhombohedrons are as follows:—

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* From ἴσος, equal, and μόρφη, shape or form.

Calcium carbonate	105° 5′
Magnesium „	107° 25′
Manganous „	107° 20′
Ferrous „	107°
Zinc „	107° 40′

Anomalies in the composition of various earthy minerals, which formerly threw much obscurity upon their chemical nature, have been in great measure explained by these discoveries. Specimens of the same mineral from different localities were found to afford very discordant results on analysis. But the proof once given of the extent to which substitution of isomorphous bodies may go, without destruction of what may be called the primitive type of the compound, these difficulties vanish.

Decision of a doubtful point respecting the constitution of a compound may sometimes be very satisfactorily made by reference to its isomorphous relations, as in the case of alumina already mentioned, which is isomorphous with the sesquioxide of iron (p. 250).

The direct determination of the crystalline forms of the elementary bodies is often difficult, and the question of their isomorphism is complicated by the frequent dimorphism which they exhibit, but when compounds are found to correspond in chemical constitution and crystalline form, it may sometimes be inferred that the elements composing them are likewise isomorphous. Thus, the metals magnesium, zinc, iron, and copper are presumed to be isomorphous. Arsenic and phosphorus have not the same crystalline form; nevertheless they are said to be isomorphous, because arsenic and phosphoric acids give rise to combinations which agree most completely in figure and constitution. The chlorides, iodides, bromides, and fluorides agree, whenever they can be observed, in the most perfect manner: hence the elements themselves are believed to be isomorphous.

The subjoined table, taken with slight modification from Graham's "Elements of Chemistry,"* will serve to convey some idea of the most important families of isomorphous elements:

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* Second edition, vol. i. p. 175.

Isomorphous Groups.

(1.
Sulphur.
Selenium
Tellurium.

(2.)
Magnesium
Calcium
Manganese
Iron
Cobalt
Nickel
Zinc
Cadmium
Copper
Chromium
Aluminium.
Glucinum.

(3.)
Barium
Strontium
Lead.

(4.)
Platinum.
Iridium
Osmium.

(5.)
Tin
Titanium
Zirconium
Tungsten
Molybdenum
Tantalum
Niobium.

(6.)
Sodium
Silver
Thallium
Gold
Potassium
Ammonium.

(7.)
Chlorine
Iodine
Bromine
Fluorine
Cyanogen.

(8.)
Phosphorus
Arsenic
Antimony
Bismuth
Vanadium.

A comparison of this table with that on page 265 will show that, in many instances, isomorphous elements exhibit equal quantivalence or combining capacity, and more generally that the isomorphous groups consist wholly of perissad or wholly of artiad elements. The only apparent exception to this rule is afforded by tantalum and niobium, which, although pentads, are isomorphous with tin, tungsten, and other tetrad and hexad elements.

CHEMICAL AFFINITY.

THE term Chemical Affinity, or Chemical Attraction, is used to describe that particular power or force, in virtue of which, union, often of a very intimate and permanent nature, takes place between two or more bodies, in such a way as to give rise to a *new* substance, having, for the most part, properties completely in discordance with those of its components.

The attraction thus exerted between different kinds of matter is to be distinguished from other modifications of attractive force which are exerted indiscriminately between all descriptions of substances, sometimes at enormous distances, sometimes at intervals quite inappreciable. Examples of the latter are to be seen in cases of which is called *cohesion*, when the particles of solid bodies are immovably bound together into a mass. Then there are other effects of, if possible, a still more obscure kind; such as the various actions of surface, the adhesion of certain liquids to glass, the repulsion of others, the ascent of water in narrow tubes, and a multitude of curious phenomena which are described in works on Physics, under the head of *molecular actions*. From all these, true chemical attraction may be at once distinguished by the deep and complete change of characters which follows its exertion: we might indeed define affinity to be a force by which new substances are generated.

It seems to be a general law that bodies most opposed to each other in chemical properties evince the greatest tendency to enter into combination; and, conversely, bodies between which strong analogies and resemblance can be traced manifest a much smaller amount of mutual attraction. For example, hydrogen and the metals tend very strongly indeed to combine with oxygen, chlorine, and iodine, but the attraction between the different members of these two groups is comparatively feeble. Sulphur and phosphorus stand, as it were, midway: they combine with substances of one and the other class, their properties separating them sufficiently from both. Acids are drawn towards alkalis, and alkalis towards acids, while union among themselves rarely if ever takes place.

Nevertheless, chemical combination graduates so imperceptibly into mere mechanical mixture, that it is often impossible to mark the limit. Solution is the result of a weak kind of affinity existing between the substance dissolved and the solvent—an affinity so feeble as completely to lose one of its most prominent features when in a more exalted condition—namely, power of causing elevation of temperature; for in the act of mere solution, the temperature falls, the heat of combination being lost and overpowered by the effects of change of state.

The force of chemical attraction thus varies greatly with the nature of the substances between which it is exerted; it is influenced, moreover, to a very large extent, by external or adventitious circumstances. An idea formerly prevailed that the relations of affinity were fixed and constant between the same substances, and great pains were taken in the preparation of tables exhibiting what was called the precedence of affinities. The order pointed out in these lists is now acknowledged to represent the order of precedence *for the circumstances* under which the experiments were made, but nothing more; so soon as these circumstances become changed, the order is disturbed. The ultimate effect, indeed, is not the result of the exercise of one single force, but rather the joint effect of a number, so complicated and so variable in intensity, that in the greater number of cases it is not possible to predict the consequences of a yet untried experiment.

It will be proper to examine shortly some of these extraneous causes to which allusion has been made, which modify to so great an extent the direct and original effects of the specific attractive force.

Alteration of temperature may be reckoned among these. When metallic mercury is heated nearly to its boiling point, and in that state exposed for a long time to the air, it absorbs oxygen, and becomes converted into a dark-red crystalline powder. This very same substance, when raised to a still higher temperature, separates spontaneously into metallic mercury and oxygen gas. It may be said, and probably with truth, that the latter change is greatly aided by the tendency of the metal to assume the vaporous state; but precisely the same fact is observed with another metal, palladium, which is not volatile, excepting at extremely high temperatures, but which oxidises superficially at a red heat, and again becomes reduced when the temperature rises to whiteness.

Insolubility and the power of vaporisation are perhaps, beyond all other disturbing causes, the most potent; they interfere in almost every reaction which takes place, and very frequently turn the scale when the opposed forces do not greatly differ in energy. It is easy to give examples. When a solution of calcium chloride is mixed with a solution of ammonium carbonate, double interchange ensues, calcium carbonate and ammonium chloride being generated: $CaCl_2 + (NH_4)_2CO_3 = CaCO_3 + 2NH_4Cl$. Here the action can be shown to be in a great measure determined by the insolubility of the calcium carbonate. On the other hand, when dry calcium carbonate is powdered and mixed with ammonium chloride, and the whole heated in a retort, a sublimate of ammonium carbonate is formed, while calcium chloride remains behind. In this instance, it is no doubt the great volatility of the new ammoniacal salt which chiefly determines the kind of decomposition.

When iron filings are heated to redness in a porcelain tube, and vapour of water is passed over them, the water undergoes decomposition with the utmost facility, hydrogen being rapidly disengaged and the iron converted into oxide. On the other hand, oxide of iron, heated in a tube through which a stream of dry hydrogen is passed, suffers almost instantaneous reduction to the metallic state, while the vapour of water, carried forward by the current of gas, escapes as a jet of steam from the extremity of the tube. In these experiments the affinities between the iron and oxygen and the hydrogen and oxygen are so nearly balanced, that the difference of *atmosphere* is sufficient to settle the point. An atmosphere of steam offers little resistance to the escape of hydrogen; an atmosphere of hydrogen bears the same relation to steam; and this apparently trifling difference of circumstances is quite enough for the purpose.

What is called the *nascent state* is one very favourable to chemical combination. Thus, nitrogen refuses to combine with gaseous hydrogen; yet when these substances are simultaneously liberated from some previous combination, they unite with great ease, as when organic matters are destroyed by heat, or by spontaneous putrefractive change.

There is a remarkable, and, at the same time, very extensive class of actions, grouped together under the general title of cases of *disposing affinity*. Metallic silver does not oxidise at any temperature: nay, more, its oxide is easily decomposed by simple heat; yet if the finely-divided metal be mixed with siliceous matter and alkali, and ignited, the whole fuses to a yellow transparent glass of silver silicate. Platinum is attacked by fused potassium hydrate, hydrogen being probably disengaged while the metal is oxidised: this is an effect which never happens to silver under the same circumstances, although silver is a much more oxidable substance than platinum. The fact is, that potash forms with the oxide of the last-named metal a kind of saline compound, in which the platinum oxide acts as an acid; and hence its formation under the *disposing* influence of the powerful base.

In the remarkable decompositions suffered by various organic bodies when heated in contact with caustic alkali or lime, we have other examples of the same fact. Products are generated which are never formed in the absence of the base; the reaction is invariably less complicated, and its reults fewer in number and more definite, than in the event of simple destruction by a graduated heat.

There is yet a still more obscure class of phenomena, called *catalytic*, in which effects are brought about by the mere *presence* of a substance which itself undergoes no perceptible change: the experiment mentioned in the chapter on oxygen, in which that gas is obtained, with the greatest facility, by heating a mixture of potassium chlorate and manganese dioxide, is a case in point. The salt is decomposed at a very far lower temperature than would otherwise be required, and yet the manganese oxide does not appear to undergo any alteration, being found after the experiment in the same state as before. It may, however, undergo a temporary alteration. We know, indeed, that this oxide when in contact with alkalis is capable of taking up an additional proportion of oxygen and forming manganic acid; and it is quite possible that in the reaction just considered it may actually take oxygen from the potassium chlorate, and pass to the state of a higher oxide, which, however, is immediately decomposed, the additional oxygen being evolved, and the dioxide returning to its original state. The same effect in facilitating the decomposition of the chlorate is produced by cupric oxide, ferric oxide, and lead oxide, all of which are known to be susceptible of higher oxidation. The oxides of zinc and magnesium, on the contrary, which do not form higher oxides, are not found to facilitate the decomposition of the chlorate; neither is any such effect produced by mixing the salt with other pulverulent substances, such as pounded glass or pure silica.

The so-called catalytic actions are often mixed up with other effects which are much more intelligible, as the action of finely divided platinum on certain gaseous mixtures, in which the solid appears to condense the gas upon its greatly extended surface, and thereby to induce combination by bringing the particles within the sphere of their mutual attractions.

Influence of Pressure on Chemical Action.—When a body is decomposed by heat in a confined space, and one or more of the separated elements (ultimate or proximate) is gaseous, the decomposition goes on until the liberated gas or vapour has attained a certain tension, greater or less according to the temperature. So long as this temperature remains constant, no further decomposition takes place, neither does any portion of the separated elements recombine: but if the temperature be raised, decomposition recommences, and goes on till the liberated gas or vapour has attained a certain higher tension, also definite for that particular temperature; if on the other hand the temperature be lowered, recomposition takes place, until the tension of the remaining gas is reduced to that which corresponds with the lower temperature. These phenomena, which are closely analogous to those exhibited in the vaporisation of liquids, have been especially studied by Deville and Debray.* Deville designates decomposition under these conditions by the term "Dissociation."

When *calcium carbonate* is heated in an iron tube, from which the air has been exhausted by means of a mercury-pump, no decomposition takes place at 300°, and a scarcely perceptible decomposition at 440°; but at 800° (in vapour of cadmium) it becomes very perceptible, and goes on till the tension of the evolved carbon dioxide becomes equivalent to 85 millimeters of mercury; there it stops so long as the temperature remains constant; but on raising the temperature to 1040° (in vapour of zinc) more carbon dioxide is

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* Watts's Dictionary of Chemistry, first Supplement, p. 425.

salts, and in the decomposition of the com
metallic chlorides, in closed spaces.

If the decomposed body, as well as one a
is gaseous, it is not possible to obtain ai
the maximum tension corresponding with
theless the decomposition is found to tak
same general law, ceasing as soon as tł
obtained a certain tension, which is great
higher.

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above a certain temperature, and that the
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to decompose at temperatures considerably
produce in the act of combining, and theref
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intensely ignited platinum. This reaction
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position takes place, but again only to a limi
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certain higher tension. The quantity of these
in this experiment is, however, very small,
them recombining as they

remains in the inner tube, and becomes mixed with carbon dioxide passing through the porous septum in the opposite direction to the hydrogen. As these gases pass through the alkaline water, the carbon dioxide is absorbed, and a mixture of hydrogen and oxygen collects in the receiver. A gram of water passed in the state of vapour through such an apparatus yields about a cubic centimeter of detonating gas.

The retarding influence of pressure is seen also in the action of acids upon zinc, or the electrolysis of water, in sealed tubes. In these cases the elimination of a gas is an essential condition of the change, and this being prevented, the action is retarded. On the other hand, there are numerous reactions which are greatly promoted by increased pressure—those, namely, which depend on the solution of gases in liquids, or on the prolonged contact of substances which under ordinary pressure would be volatilised by heat.

Relations of Heat to Chemical Affinity.—Whatever may be the real nature of chemical affinity, one most important fact is clearly established with regard to it; namely, that its manifestations are always accompanied by the production or annihilation of heat. Change of composition, or chemical action, and heat are mutually convertible: a given amount of chemical action will give rise to a certain definite amount of heat, which quantity of heat must be directly or indirectly expended, in order to reverse or undo the chemical action that has produced it. The production of heat by chemical action, and the definite quantitative relation between the amount of heat evolved and the quantity of chemical action which takes place, are roughly indicated by the facts of our most familiar experience; thus, for instance, the only practically important method of producing heat artificially consists in changing the elements of wood and coal, together with atmospheric oxygen, into carbon dioxide and water; and every one knows that the heat thus obtainable from a given quantity of coal is limited, and is, at least approximately, always the same. The accurate measurement of the quantity of heat produced by a given amount of chemical action is a problem of very great difficulty; chiefly because chemical changes very seldom take place alone, but are almost always accompanied by physical changes, involving further calorimetric effects, each of which requires to be accurately measured and allowed for, before the effect due to the chemical action can be rightly estimated. Thus the ultimate result has, in most cases, to be deduced from a great number of independent measurements, each liable to a certain amount of error. It is therefore not surprising that the results of various experiments should differ to a comparatively great extent, and that some uncertainty should still exist as to the exact quantity of heat corresponding with even the simplest cases of chemical action.

The experiments are made by enclosing the acting substances in a vessel called a calorimeter, surrounded by water or mercury,

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involve details which are beyond the lim

The following table gives the quanti
heat-units,† evolved in the combustion o
few compounds, in oxygen, referred : (1) t
burned ; (2) to 1 gram of oxygen consun
molecule (expressed in grams), of the varic

Heat of Combustion of Elementary Su

Substance.	Product.	Units of heat e	
		By 1 gram of substance.	By 1 gram of oxygen.
Hydrogen . .	H_2O	33881 34462	4235 4308
Carbon—			
Wood-charcoal .	CO_2	7900 8080	2962 3030
Gas-retort carbon	,,	8047	3018
Native graphite .	,,	7797	2924
Artificial graphite	,,	7762	2911
Diamond . .	,,	7770	2914
Sulphur—			
Native . .	SO_2	2220	2220
Recently melted .	,,	2260	2260
Flowers . .	,,	2307	2307
Phosphorus—			
(Yellow) . .	P_2O_5	5747	[illegible]
Zinc			

The following results have been obtained by the complete combustion of partially oxidised substances :—

Substance.	Product.	Units of heat evolved.		Observer.
		By 1 gram of substance.	In formation of 1 molecule of the ultimate product.	
Carbon monoxide, CO . . .	CO_2	2403	67284	Favre & Silbermann.
		2431	68064	Andrews.
Stannous oxide, SnO	SnO_2	519	69584	,,
Cuprous oxide, Cu_2O	CuO	256	18304	,,

The last three substances in this table contain exactly half as much oxygen as the completely oxidised products ; and on comparing the amount of heat evolved in the formation of one molecule of stannic or cupric oxide from the corresponding lower oxide, with the quantity produced when a molecule of the same product is formed by the complete oxidation of the metal in one operation, we find that the combination of the second half of the oxygen contained in these bodies evolves sensibly half as much as the combination of the whole quantity. In the formation of carbon dioxide, however, the second half of the oxygen appears to develop more than two-thirds of the total amount of heat ; but this result is probably due, in part at least, to the fact that when carbon is burned into carbon dioxide, a considerable but unknown quantity of heat is expended in converting the solid carbon into gas, and thus escapes measurement ; while, in carbon monoxide, the carbon already exists in the gaseous form, and therefore no portion of the heat evolved in the combustion of this substance is similarly expended in producing a change of state.

It seems probable, also, that a similar explanation may be given of the inequalities in the quantities of heat produced by the combustion of different varieties of pure carbon and of sulphur—that is to say, that a portion of the heat generated by the combustion of diamond and graphite goes to assimilate their molecular condition to that of wood-charcoal, and that there is an analogous expenditure of heat in the combustion of native sulphur.

The quantities of heat evolved in the combination of chlorine, bromine, and iodine with other elements have been determined by Favre and Silbermann, Andrews, and others ; but we must refer to larger works for the results.*

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* Watts's Dictionary of Chemistry, iii. 109.

Reactions in Presence of Water.—The thermal effects which may result from the reaction of different substances on one another in presence of water, are more complicated than those resulting from direct combination. In addition to the different specific heats of the re-agents and products, and to the different quantities of heat absorbed by them in dissolving, or given out by them in combining with water, the conversion of soluble substances into insoluble ones, as a consequence of the chemical action, or the inverse change of insoluble into soluble bodies, are among the secondary causes to which part of the calorimetric effect may be due in these cases.

When a gas dissolves in water, the heat due to the chemical action is augmented by that due to the liquefaction of the gas; so also when a solid body is dissolved in water, the total thermal effect is due in part to the chemical action taking place between the water and the solid, and in part to the liquefaction of the substance dissolved. In the former case the chemical and physical parts of the phenomena both cause evolution of heat; in the latter case the physical change occasions disappearance of heat, and if this effect is greater than that due to the chemical action, the ultimate effect is the production of cold, and it is this which is generally observed.

Cold produced by Chemical Decomposition.—It is highly probable that the thermal effect of the reversal of a given chemical action is in all cases equal and opposite to the thermal effect of that action itself. *A direct consequence of this proposition is that the separation*

ELECTRO-CHEMICAL DECOMPOSITION; CHEMISTRY OF THE VOLTAIC PILE.

When a voltaic current of considerable power is made to traverse various compound liquids, a separation of the elements of these liquids ensues: provided that the liquid be capable of conducting the current, its decomposition almost always follows.

The elements are disengaged solely at the limiting surfaces of the liquid, where, according to the common mode of speech, the current enters and leaves the latter, all the intermediate portions appearing perfectly quiescent. In addition, the elements are not separated indifferently and at random at these two surfaces; but, on the contrary, make their appearance with perfect uniformity and constancy at one or the other, according to their chemical character, namely, oxygen, chlorine, iodine, acids, &c., at the surface connected with the *copper*, or *positive* end of the battery; hydrogen, the metals, &c., at the surface in connection with the *zinc*, or *negative* extremity of the arrangement.

The terminations of the battery itself—usually, but by no means necessarily, of metal—are designated poles or *electrodes*,* as by their intervention the liquid to be experimented on is made a part of the circuit. The process of decomposition by the current is called *electrolysis*,† and the liquids, which, when thus treated, yield up their elements, are denominated *electrolytes*.

When a pair of platinum plates are plunged into a glass of water to which a few drops of oil of vitriol have been added, and the plates connected by wires with the extremities of an active battery, oxygen is disengaged at the positive electrode, and hydrogen at the negative, in the proportion of one measure of the former to two of the latter nearly. This experiment has already been described.‡

A solution of hydrochloric acid mixed with a little Saxon blue (indigo), and treated in the same manner, yields hydrogen on the negative side and chlorine on the positive, the indigo there becoming bleached.

Potassium iodide dissolved in water is decomposed in a similar manner: the free iodine at the positive side can be recognised by its brown colour, or by the addition of a little gelatinous starch.

All liquids are not electrolytes; many refuse to conduct, and no decomposition can then occur; alcohol, ether, numerous essential oils, and other products of organic chemistry, besides a few saline inorganic compounds, act in this manner, and completely arrest the current of a powerful battery.

One of the most important and indispensable conditions of electrolysis is fluidity; bodies which, when reduced to the liquid state, conduct freely, and as freely suffer decomposition, become absolute insulators to the electricity of the battery when they become solid. Lead chloride offers a good illustration of this fact: when fused in a porcelain crucible, it gives up its elements with the utmost ease, and a galvanometer, interposed in the circuit, is strongly affected. But when the source of heat is withdrawn, and the salt suffered to solidify, signs of decomposition cease, and at the same moment the magnetic needle reassumes its natural position. In the same manner, the thinnest film of ice arrests the current of a powerful voltaic apparatus; but the instant the ice is liquefied, so that water communication is restored between the electrodes, the current again passes, and decomposition occurs. Fusion by heat, and solution in aqueous liquids, answer the purpose equally well.

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* From ἤλεκτρον, and ὁδός, a way.

† From ἤλεκτρον, and λύειν, to loose.

‡ Page 138.

Generally speaking, compound liquids cannot conduct the electric current without being decomposed; but still there are a few exceptions to this statement, which perhaps are more apparent than real. Thus Hittorf has shown that fused silver sulphide, which was formerly regarded as one of the exceptions, cannot be considered to be so, and Beetz has since proved the same to be the case as regards mercuric iodide and lead fluoride.

The quantity of any given compound liquid which can be decomposed by any given electric battery depends on the resistance of the liquid: the more resistance the less decomposition. Distilled water has only a small power of conduction, and is therefore only slightly decomposed by a battery of 30 to 40 pairs; whilst diluted sulphuric acid is one of the best of fluid conductors, and undergoes rapid decomposition by a small battery.

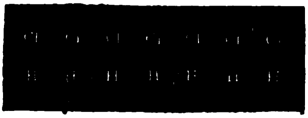
When a liquid which can be decomposed, and a galvanometer, are included in the circuit of an electric current, if the needle of the galvanometer be deflected, it may be always assumed as certain that a portion of liquid, bearing a proportion to the strength of the current, is decomposed, although it may be impossible in many cases, without special contrivances, to detect the products of the decomposition, on account of their minuteness.

The metallic terminations of the battery, the poles or electrodes, have, in themselves, nothing in the shape of attractive or repulsive power for the elements separated at their surfaces. Finely divided metal suspended in water, or chlorine held in solution in that liquid, shows not the least symptom of a tendency to accumulate around them; a single element is altogether unaffected—directly, at least; separation from previous combination is required, in order that this appearance should be exhibited.

It is necessary to examine the process of electrolysis a little more closely. When a portion of hydrochloric acid, for example, is subjected to decomposition in a glass vessel with parallel sides, chlorine is disengaged at the positive electrode, and hydrogen at the negative: the gases are perfectly pure and unmixed. If, while the decomposition is rapidly proceeding, the intervening liquid be examined by a beam of light, or by other means, not the slightest disturbance or movement of any kind will be perceived; nothing like currents in the liquid or bodily transfer of gas from one part to another can be detected; and yet two portions of hydrochloric acid, separated perhaps by an interval of four or five inches, may be respectively evolving pure chlorine and pure hydrogen.

There is, it would seem, but one mode of explaining this and all similar cases of regular electrolytic decomposition: this is by assuming that *all* the particles of hydrochloric acid between the electrodes, and by which the current is conveyed, simultaneously suffer decomposition, the hydrogen travelling in one direction, and the chlorine in the other. The neighbouring elements, thus brought into close proximity, unite and reproduce hydrochloric acid, again destined to be decomposed by a repetition of the same change. In this manner each particle of hydrogen may be made to travel in one direction, by becoming successively united to each particle of chlorine between itself and the negative electrode; when it reaches the latter, finding no disengaged particle of chlorine for its reception, it is rejected, as it were, from the series, and thrown off in a separate state. The same thing happens to each particle of chlorine, which at the same time passes continually in the opposite direction, by combining successively with each particle of hydrogen, that moment separated, with which it meets, until at length it arrives at the positive plate or wire, and is disengaged. A succession of particles of hydrogen is thus continually thrown off from the decomposing mass at one extremity, and a corresponding succession of particles of chlorine at the other. The power of the current is exerted with equal energy in every part of the liquid conductor, though its effects become manifest only at the very extremities. The action is one of a purely molecular or internal nature, and the metallic terminations of the battery merely serve the purpose of completing the connection between the latter and the liquid to be decomposed.

Fig. 132.



Hydrochloric acid in its usual state.

Fig. 133.

Hydrochloric acid undergoing electrolysis.

The figures 132 and 133 are intended to assist the imagination of the reader, who must at the same time avoid regarding them in any other light than that of a somewhat figurative mode of representing the phenomena described. The circles are intended to indicate the elements, and are distinguished by their respective symbols.

Like hydrochloric acid, all electrolytes, when acted on by electricity, are split into two constituents, which pass in opposite directions. Substances of the one class, like oxygen, chlorine, &c., are evolved at the positive electrode; those of the other class, like hydrogen and the metals, at the negative electrode.

It is of importance to remark that oxygen-salts, such as sulphates and nitrates, when acted on by the current, do not divide into acid and basic oxide, but, as Daniell and Miller proved, into metal and a compound substance, or group of elements, which is transferred in such a state of association that, as regards its electrical behaviour, it represents an element. Thus, cupric sulphate, $CuSO_4$, splits, not into SO_3 and CuO, but into metallic copper and *sulphione*, SO_4. Hydrogen sulphate, or sulphuric acid, H_2SO_4, divides into the same compound group and hydrogen. In a similar way, also, the part of the electrolyte which passes to the negative pole may consist of a group of elements. A solution of sal-ammoniac, NH_4Cl, furnishes a beautiful instance of this fact, since it is decomposed by the current in such a manner that the ammonium, NH_4, goes to the negative pole, where it is resolved into ammonia, NH_3, and free hydrogen, and the chlorine to the positive pole.

A distinction must be carefully drawn between true and regular electrolysis, and what is called secondary decomposition, brought about by the reaction of the bodies so eliminated upon the surrounding liquid, or upon the substance of the electrodes: hence the advantage of platinum for the latter purpose, when electrolytic actions are to be studied in their greatest simplicity, that metal being scarcely attacked by any ordinary agents. When, for example, a solution of lead nitrate or acetate is decomposed by the current between platinum plates, metallic lead is deposited at the negative side, and a brown powder, lead dioxide, at the positive: the latter substance is the result of a secondary action; it proceeds, in fact, from the nascent oxygen, at the moment of its liberation, reacting upon the monoxide of lead present in the salt, and converting it into dioxide, which is insoluble in the dilute acid. When nitric acid is decomposed, no hydrogen appears at the negative electrode, because it is oxidised at the expense of the acid, which is reduced to nitrous acid. When potassium sulphate, K_2SO_4, is electrolysed, hydrogen appears at the negative electrode, together with an equivalent quantity of potassium hydroxide, KHO, because the potassium which is evolved at the electrode immediately decomposes the water there present. At the same time, the sulphione, SO_4, which is transferred to the positive electrode, takes hydrogen from the water there present, forming sulphuric acid, H_2SO_4, and liberating oxygen. In like manner hydrogen sulphate, or sulphuric acid itself, is resolved by the current into hydrogen and sulphione, which latter decomposes the water at the positive electrode, reproducing hydrogen sulphate, and liberating oxygen, just as if the water itself were directly decomposed by the current into hydrogen and oxygen. A similar action takes place in the electrolytic decomposition of any other oxygen salt of an alkali-metal, or alkaline earth-metal, alkali and hydrogen gas making their appearance at the negative electrode, acid and oxygen gas at the positive electrode. This observation explains a circumstance which much perplexed the earlier experimenters upon the chemical action of the voltaic battery. In all experiments in which water was decomposed, both acid and alkali were liberated at the electrodes, even though distilled water was employed; and hence it was believed for some time that the voltaic current had some mysterious power of generating acid and alkaline matter. The true source of these compounds was, however, traced by Davy,[*] who showed that they proceeded from impurities either in the water itself, or in the vessels which contained it, or in the surrounding atmosphere. Having proved that ordinary distilled water always contains traces of saline matter, he redistilled it at a temperature below the boiling point, in order to avoid all risk of carrying over salts by splashing. He then found that when marble cups were used to contain the water used for decomposition, hydrochloric acid appeared at the positive electrode, soda at the negative, both being derived from sodium chloride present in the marble; when agate cups were used, he obtained silica; and when he used gold vessels, he obtained nitric acid and ammonia, which he traced to atmospheric air. By operating in a vacuum, indeed, the quantity of acid and alkali was reduced to a minimum, but the decomposition was almost arrested, although he operated with a battery of fifty pairs of 4-inch plates. Hence it is manifest that *water itself is not an electrolyte*, but that it is enabled to convey the current if it contains only traces of saline matter.[†]

Definite Chemical Action of the Electric Current.—If a number of different electrolytes, such as dilute sulphuric acid, cupric sulphate, potassium iodide, fused lead chloride, &c., be arranged in a series, and the same current be made to traverse the whole, all will suffer decomposition at the same time, but by no means to the same amount. If arrangements be made by which the quantities of the eliminated elements can be accurately ascertained, it will be found, when the decomposition has proceeded to some extent, that these latter have been disengaged exactly in the *ratio of their chemical equivalents*. The same current which decomposes 9 parts of water will separate into their elements 166 parts of potassium iodide, 139 parts of lead chloride, &c. Hence the very important conclusion: *The action of the current is perfectly definite in its nature, producing a fixed and constant amount of decomposition, expressed in each electrolyte by the value of its chemical equivalent.*

From a very extended series of experiments, based on this and other methods of research, Faraday was enabled to draw the general inference that effects of chemical decomposition are always proportionate to the quantity of circulating electricity, and may be taken as an accurate and trustworthy measure of the latter. Guided by this highly important principle, he constructed his *voltameter*, an instrument which has rendered the greatest service to electrical science. This is merely an arrangement by which dilute sulphuric acid is decomposed by the current, the gas evolved being collected and measured. By placing such an instrument in any part of the circuit, the quantity of electric force necessary to produce any given effect can be at once estimated; or, on the other hand, any required amount of the latter can be, as it were, measured out and adjusted to the object in view. The voltameter has received many different forms: one of the most extensively useful is that shown in fig. 134, in which the platinum plates are separated by a very small interval, and the gas is collected in a graduated jar standing on the shelf of the pneumatic trough, the tube of the instrument, which is filled to the neck with dilute sulphuric acid, being passed beneath the jar.

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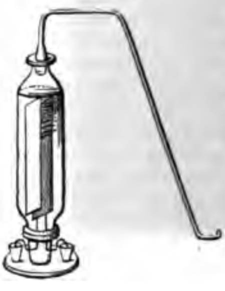
[*] Philosophical Transactions, 1807.

[†] Miller's Chemical Physics, p. 484.

Fig. 134.



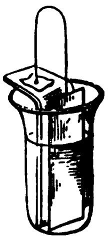
The decompositions produced by the voltaic battery can be effected by the electricity of the common machine, by that developed by magnetic action, and by that of animal origin, but to an extent incomparably more minute. This arises from the very small *quantity* of electricity set in motion by the machine, although its *tension*—that is, power of overcoming obstacles, and passing through imperfect conductors—is exceedingly great. A pair of small wires of zinc and platinum, dipping into a single drop of dilute acid, develops far more electricity, to judge from the chemical effects of such an arrangement, than very many turns of a large plate electrical machine in powerful action. Nevertheless, polar or electrolytic decomposition can be distinctly and satisfactorily effected by the latter, although on a minute scale.

Theory of the Voltaic Battery.—With a knowledge of the principles just laid down, the study of the voltaic battery may be resumed and completed. In the first place, two very different views have been held concerning the source of the electrical disturbance in that apparatus. Volta himself ascribed it to mere contact of dissimilar metals or other substances conducting electricity,—to what was denominated an *electro-motive* force, called into being by such contact. Proof was supposed to be given of this fundamental proposition by an experiment in which discs of zinc and copper attached to insulating handles, after being brought into close contact, were found, by the aid of a very delicate gold-leaf electroscope, to be in opposite electrical states. It appears, however, that the more carefully this experiment is made, the smaller is the effect observed; and hence it is judged highly probable that the whole may be due to accidental causes, against which it is almost impossible to guard.

On the other hand, the observation was soon made that the power of the battery always bears some kind of proportion to the chemical action upon the zinc; that, for instance, when pure water is used, the effect is extremely feeble; with a solution of salt, it becomes much greater; and, lastly, with dilute acid, greatest of all; so that some relation evidently exists between the chemical effect upon the metal and the evolution of electrical force.

The experiments of Faraday and Daniel have given very great support to the chemical theory, by showing that the contact of dissimilar metals is *not* necessary in order to call into being powerful electrical currents, and that the development of electrical force is not only in some way connected with the chemical action of the liquid of the battery, but that it is always in direct proportion to the latter. One very beautiful experiment, in which electrolytic decomposition of potassium iodide is performed by a current generated without any contact of dissimilar metals, can be thus made:—A plate of zinc is bent at a right angle, and cleaned by rubbing with sand-paper. A plate of platinum has a wire of the same metal attached to it by careful riveting, and the wire is bent into an arch. A piece of folded filter-paper is wetted with solution of potassium iodide, and placed upon the zinc; the platinum plate is arranged opposite to the latter, with the end of its wire resting upon the paper; and then the pair is plunged into a glass of dilute sulphuric, mixed with a few drops of nitric acid. A brown spot of iodine becomes in a moment evident beneath the extremity of the platinum wire—that is, at the positive side of the arrangement.

Fig. 135.



A strong argument in favour of the chemical view is founded on the easily proved fact, that the direction of the current is determined by the kind of action upon the metals, the one least attacked being always positive. Let two polished plates, the one iron and the other copper, be connected by wires with a galvanometer, and then immersed in a solution of an alkaline sulphide. The needle in a moment indicates a powerful current, passing from the copper through the liquid to the iron, and back again through the wire. Let the plates be now removed, cleaned, and plunged into dilute acid; the needle is again driven round, but in the opposite direction, the current now passing from the iron through the liquid to the copper. In the first instance, the copper is acted upon, and not the iron; in the second, these conditions are reversed, and with them the direction of the current.

The metals employed in the construction of voltaic batteries are zinc for the active metal, and copper, silver, or, still better, platinum, for the inactive one: the greater the difference of oxidability, the better the arrangement. The liquid is either dilute sulphuric acid, sometimes mixed with a little nitric, or occasionally, where very slow and long-continued action is wanted, salt and water. To obtain the maximum effect of the apparatus with the least expenditure of zinc, that metal must be employed in a pure state, or its surface must be covered with an amalgam, which in its electrical relations closely resembles the pure metal. The zinc is easily brought into this condition by wetting it with dilute sulphuric acid, and then rubbing a little mercury over it, by means of a piece of rag tied to a stick.

The principle of the compound battery is, perhaps, best seen in the crown of cups: by each alternation of zinc, fluid, and copper, the current is urged forwards with increased energy; its intensity is augmented, but the actual amount of electrical force thrown into the current form is not increased. The quantity, estimated by its decomposing power, is, in fact, determined by that of the smallest and least active pair of plates, the quantity of electricity in every part or section of the circuit being exactly equal. Hence large and small plates, batteries strongly and weakly charged, can never be connected without great loss of power.

When a battery, either simple or compound, constructed with pure or with amalgamated zinc, is charged with dilute sulphuric acid, a number of highly interesting phenomena may be observed. While the circuit remains broken, the zinc is perfectly inactive, no acid is decomposed, no hydrogen liberated; but the moment the connection is completed, torrents of hydrogen arise, not from the zinc, but from the copper or platinum surfaces alone, while the zinc undergoes tranquil and imperceptible oxidation and solution. Thus, exactly the same effects are seen to occur in every active cell of a closed circuit, that are witnessed in a portion of sulphuric acid undergoing electrolysis: oxygen appears at the positive side, with respect to the current, and hydrogen at the negative; but with this difference, that the oxygen, instead of being set free, combines with the zinc. It is, in fact, a real case of electrolysis, and electrolytes alone are available as exciting liquids.

Common zinc is very readily attacked and dissolved by dilute sulphuric acid; and this is usually supposed to arise from the formation of a multitude of little voltaic circles, by the aid of particles of foreign metals or graphite, partially imbedded in the zinc. This gives rise in the battery to what is called local action, by which, in the common forms of apparatus, three-fourths or more of the metal is often consumed, without contributing in the least to the general effect, but, on the contrary, injuring it to some extent. This evil is got rid of by amalgamating the surface.

By careful experiments, in which local action was completely avoided, it has been distinctly proved that the quantity of electricity set in motion by the battery varies exactly with the zinc dissolved. Coupling this fact with that of the definite action of the current, it will be seen that when a perfect battery of this kind is employed to decompose hydrochloric acid, in order to evolve 1 grain of hydrogen from the latter, 32·5 grains of zinc must be dissolved as chloride, and its equivalent quantity of hydrogen disengaged in each active cell of the battery—that is to say, that the electrical force generated by the solution of an equivalent of zinc *in* the battery is capable of effecting the decomposition of an equivalent of hydrochloric acid or any other electrolyte *out* of it.

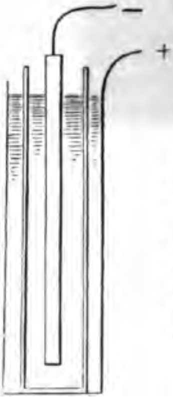
This is an exceedingly important discovery: it serves to show, in the most striking manner, the intimate nature of the connection between chemical and electrical forces, and their remarkable quantitative or equivalent relations. It almost seems, to use an expression of Farady, as if a transfer of chemical force took place through the substance of solid metallic conductors; that chemical actions, called into play in one portion of the circuit, could be made at pleasure to exhibit their effects without loss or diminution in any other.

Electro-chemical Theory.—There is an hypothesis, not of recent date, long countenanced and supported by the illustrious Berzelius, which refers all chemical phenomena to electrical forces—which supposes that bodies combine because they are in opposite electrical states; and that even the heat and light accompanying chemical union may be, to a certain extent, accounted for in this manner; that, in short, so far as our present knowledge goes, either electric or chemical action may be assumed as cause or effect: it may be that electricity is merely a form or modification of ordinary chemical affinity; or, on the other hand, that all chemical action is a manifestation of electrical force.

This electro-chemical theory is no longer received as a true explanation of chemical phenomena to the full extent intended by its author. Berzelius, indeed, supposed that the combining tendencies of elements, and their functions in compounds, depend altogether on their electric polarity; and accordingly he divided the elements into two classes, the electro-positive, which like hydrogen and the metals, move towards the negative pole of the battery, as if they were attracted by it, and the electro-negative, which, like oxygen, chlorine, and bromine, move towards the positive pole. We are, however, acquainted with a host of phenomena which show that the chemical functions of an element depend upon its position with regard to other elements in a compound, quite as much as upon its individual character. Thus chlorine, the very type of an electro-negative element, can be substituted for hydrogen, one of the most positive of the elements, in a large number of compounds, yielding new products, which exhibit the closest analogy in composition and properties to the compounds from which they are derived. It is impossible, therefore, to admit that the chemical functions of bodies are determined exclusively by their electrical relations. Still it is true in a general way that those elements which differ most strongly in their electrical characters, chlorine and potassium, for example, are likewise those which combine together with the greatest energy; and the division of bodies into electro-positive and electro-negative is therefore retained; the former are also called acid or chlorous, and the latter basylous or zincous.

Constant Batteries.—In all the older forms of the voltaic battery, such as those described on pages 105, 106, the power rapidly decreases, so that, after a short time, scarcely the tenth part of the original action remains. This loss of power depends, partly on the gradual change of the sulphuric acid into zinc sulphate, but still more on the coating of hydrogen, and, at a later stage, on the precipitation of metallic zinc on the copper plates. It is self-evident that if the copper plate in the liquid became covered with zinc, it would act electrically like a zinc plate.

Fig. 136.



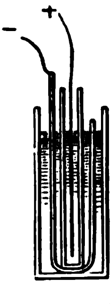
An apparatus of immense value for purposes of electro-chemical research, in which it is desired to maintain powerful and equable currents for many successive hours, was contrived by the late Professor Daniell (fig. 136). Each cell of this "constant" battery consists of a copper cylinder 3½ inches in diameter, and of a height varying from 6 to 18 inches. The zinc is employed in the form of a rod ¾ of an inch in diameter, carefully amalgamated, and suspended in the centre of the cylinder. A second cell of porous earthenware or animal membrane intervenes between the zinc and the copper: this is filled with a mixture of 1 part by measure of oil of vitriol and 8 of water, and the exterior space with the same liquid saturated with copper sulphate. A sort of little colander is fitted to the top of the cell, in which crystals of the copper sulphate are placed, so that the strength of the solution may remain unimpaired. When a communication is made by a wire between the rod and the cylinder, a strong current is produced, the power of which may be increased to any extent by connecting a sufficient number of such cells into a series, on the principle of the crown of cups, the copper of the first being attached to the zinc of the second. Ten such alterations constitute a very powerful apparatus, which has the great advantage of retaining its energy undiminished for a long time.

By this arrangement of the voltaic battery, the accumulation of hydrogen and deposition of zinc on the surface of the copper plate is altogether avoided; the zinc in the porous cell, whilst it dissolves in the sulphuric acid, decomposes it, but does not liberate any hydrogen; for by the progress of the decomposition (see p. 289), up to the boundary of the copper solution, the hydrogen takes the place of the copper, and thus ultimately the copper is precipitated on the copper plate. The copper plate therefore remains in its original state, so long as a sufficient quantity of copper sulphate is present in the solution.

By increasing the generative and reducing the antagonising chemical affinities, Mr. Grove succeeded in forming the constant nitric acid battery which bears his name. This instrument is capable of producing a far greater degree of power than the battery previously mentioned, and hence it has become one of the most important means of promoting electrical science in the present day. The zinc dips into dilute sulphuric acid; and instead of a solution of copper, concentrated nitric acid is used, which surrounds a platinum plate. It is evident that the electrolytic action which begins at the zinc passes through the sulphuric acid, and in a precisely similar way through the contiguous nitric acid. Hydrogen would thus be liberated on the platinum plate. This action is not rendered visible by the evolution of gas, but only gradually by the change of colour in the nitric acid: for the hydrogen liberated by the electrical action forms water at the expense of the oxygen yielded by the nitric acid; and by this means, so long as sufficient nitric acid is present, the purity of the surface of the platinum plate is maintained.

One of the cells in this battery is represented in section in fig. 137. The zinc plate is bent round, so as to present a double surface, and well amalgamated: within it stands a thin flat cell of porous earthenware, filled with strong nitric acid, and the whole is immersed in a mixture of 1 part by measure of oil of vitriol and 6 of water, contained either in one of the cells of Wollaston's trough, or in a separate cell of glazed porcelain, made for the purpose. The apparatus is completed by a plate of platinum foil, which dips into the nitric acid, and forms the positive side of the arrangement. With ten such pairs, experiments of decomposition, ignition of wires, the light between charcoal points, &c., can be exhibited with great brilliancy, while the battery itself is very compact and portable, and, to a great extent, constant in its action. The zinc, as in the case of Daniell's battery, is consumed only while the current passes, so that the apparatus may be arranged an hour or two before it is required for use, which is often a matter of great convenience; and local action from the precipitation of copper on the zinc is avoided.

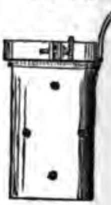
Fig. 137.



Professor Bunsen has modified the Grove battery by substituting for the platinum, dense charcoal or coke, which is an excellent conductor of electricity. By this alteration, at a very small expense, a battery may be made nearly as powerful and useful as that of Grove. On account of its cheapness, any one may put together one hundred or more of Bunsen's cells, by which the most magnificent phenomena of heat and light may be obtained.

Figure 138 shows the form of the round carbon cylinder which is used in these cells. It is hollowed so as to receive a porous earthenware cell, in which a round plate of zinc is placed. The upper edge of the cylinder of carbon is well saturated with wax, and is surrounded by a copper ring, by means of which it may be put in connection with the zinc of the adjoining pair.

Fig. 138.



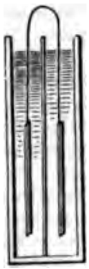
Bunsen's carbon cylinder is likewise well adapted for the use of dilute sulphuric acid alone, without the addition of nitric acid. It is, however, better to saturate the dilute sulphuric acid with potassium bichromate. When this mixture contains at least double the amount of sulphuric acid which is necessary to decompose the chromate, a battery is formed which surpasses in power the nitric acid battery, but does not furnish currents of the same constancy.

Mr. Smee has contrived an ingenious battery, in which silver, covered with a thin coating of finely divided metallic platinum, is employed in association with amalgamated zinc and dilute sulphuric acid. The rough surface appears to permit the ready disengagement of the bubbles of hydrogen.

Gas-battery.—Mr. Grove has contrived a battery in which an electrical current, of sufficient intensity to decompose dilute sulphuric acid, is produced by the action of oxygen upon hydrogen. Each *element* of this apparatus consists of a pair of glass tubes to contain the gases, dipping into a vessel of acidulated water. Both tubes contain platinum plates, covered with a rough deposit of finely divided platinum, and furnished with conducting wires, which pass through the tops or sides of the tubes, and are hermetically sealed into the latter. When the tubes are charged with oxygen on the one side and hydrogen on the other, and the wires connected with a galvanoscope, the needle of the instrument becomes instantly affected; and when ten or more are combined in a series, the oxygen-tube of the one with the hydrogen-tube of the next, &c., while the terminal wires dip into acidulated water, a rapid stream of minute bubbles from either wire indicates the decomposition of the liquid; and when the experiment is made with a small voltameter, it is found that the oxygen and hydrogen disengaged exactly equal in amount the quantities absorbed by the act of combination in each tube of the battery.

Electrotype.—Within the last forty years, several very beautiful and successful applications of voltaic electricity have been made, which may be slightly mentioned. Mr. Spencer and Professor Jacobi have employed it in copying, or rather in multiplying, engraved plates and medals, by depositing upon their surfaces a thin coating of metallic copper, which when separated from the original, exhibits, in reverse, a most faithful representation of the latter. By using this in its turn as a mould or matrix, an absolutely perfect *fac-simile* of the plate or medal is obtained. In the former case, the impressions taken on paper are quite undistinguishable from those directly derived from the work of the artist; and as there is no limit to the number of *electrotype* plates which can be thus produced, engravings of the most beautiful description may be multiplied indefinitely. The copper is very tough, and bears the action of the press perfectly well.

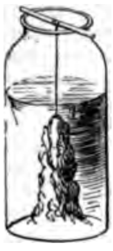
Fig. 139.



The apparatus used in this and many similar processes is of the simplest kind. A trough or cell of wood is divided by a porous diaphragm, made of a very thin piece of sycamore, into two parts; dilute sulphuric acid is put on one side, and a saturated solution of copper sulphate, sometimes mixed with a little acid, on the other. A plate of zinc is soldered to a wire or strip of copper, the other end of which is secured by similar means to the engraved copper plate. The latter is then immersed in the solution of sulphate, and the zinc in the acid. To prevent deposition of copper on the back of the copper plate, that portion is covered with varnish. For medals and small works, a porous earthenware cell, placed in a jelly-jar, may be used.

Other metals may be precipitated in the same manner, in a smooth and compact form, by the use of certain precautions which have been gathered by experience. Electro-gilding and plating are now carried on very largely and in great perfection by Messrs. Elkington and others. Even non-conducting bodies, as sealing-wax and plaster of Paris, may be coated with metal; it is only necessary, as shown by the late Mr. Robert Murray, to rub over them the thinnest possible film of plumbago. Seals may thus be copied in a very few hours with unerring truth.

Fig. 140.



The common but very pleasing experiment of the *lead-tree* is greatly dependent on electro-chemical action. When a piece of zinc is suspended in a solution of lead acetate, the first effect is the decomposition of a portion of the latter, and the deposition of metallic lead upon the surface of the zinc; it is simply a displacement of a metal by a more oxidable one. The change does not, however, stop here; metallic lead is still deposited in large and beautiful plates upon that first thrown down, until the solution becomes exhausted, or the zinc entirely disappears. The first portions of lead form with the zinc a voltaic arrangement of sufficient power to decompose the salt: under the peculiar circumstances in which the latter is placed, the metal is precipitated upon the negative portion—that is, the lead—while the oxygen and acid are taken up by the zinc.

Becquerel, several years ago, published an exceedingly interesting account of certain experiments in which crystallised metals, oxides, and other insoluble substances had been produced by the slow and continuous action of feeble electrical currents, kept up for months, or even years. These products exactly resemble natural minerals: and, indeed, the experiments throw great light on the formation of the latter within the earth.[*]

Heat developed by the Electric Current.—All parts of the electric circuit, the plates, the liquid in the cells of the battery, the conducting wires, and any electrolytes undergoing decomposition, all become heated during the passage of the current. The rise of temperature in any part of the circuit depends partly on the strength of the current, partly on its resistance, those bodies which offer the greatest resistance, or are the worst conductors, being most strongly heated by a current of given strength. Thus, when a thick and a thin wire of the same metal are included in the same circuit, the latter becomes most strongly heated, and a platinum wire is much more strongly heated than a silver or copper wire of the same thickness.

By exact experiments it has been found that both in metallic wires and in liquids traversed by an electric current, the evolution of heat is directly proportional—1st, *to the resistance;* 2d, *to the strength of the current.* Joule has[†] also shown that the evolution of heat in each couple of the voltaic battery is subject to the same law, which, therefore, holds good in every part of the circuit, including the battery.

The strength of an electric current is measured by the quantity of detonating gas (2 vols. H to 1 vol. O) which it can evolve from acidulated water in a given time, and the *unit of current strength is the current which eliminates one cubic centimeter of detonating gas at* 0° C. and $760^{\text{mm.}}$ *barometric pressure in a minute.* Now Lenz has shown that when a current of the unit of strength passes through a wire whose resistance is equal to that of a copper wire 1 meter long and 1 millimeter in diameter, it develops a quantity of heat sufficient to raise the temperature of 1 gram of water from 0° to 1° C. in 5¾ minutes; and assuming as the unit of heat the quantity required to raise the temperature of 1 gram of water from 0° to 1° C., the law may be thus expressed—

A current of the unit of strength passing through a conductor which exerts the unit of resistance, develops therein 1·057 *heat-unit in an hour, or* 0·0176 *heat-unit in a minute.*

With a current of given strength, the sum of the quantities of heat evolved in the battery and in the metallic conductor joining its poles, is constant, the heat actually developed in the one part or the other varying according to the thickness of the metallic conductor. This was first shown by De la Rive, and has been confirmed by Favre.* De la Rive made use of a couple consisting of platinum and distilled zinc or cadmium, excited by pure and very strong nitric acid, the two metals being united by a platinum wire, more or less thick, which was plunged into the same quantity of strong nitric acid contained in a capsule, similar to that which held the voltaic couple. By observing the temperatures in the two vessels with delicate thermometers, the sum of these temperatures was found to be constant, the one or the other being greater according to the thickness of the connecting wire.

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[*] Traité de l'Electricité et du Magnétisme, iii. 239.

[†] Phil. Mag. [3] xix. 210.

Favre,† by means of a calorimeter, similar to that which he used in his experiments on the development of heat by chemical action, has shown that in a pair of zinc and platinum plates, excited by dilute sulphuric acid and connected by platinum wires of various length and thickness, for every 32·5 grams of zinc dissolved, a quantity of heat is developed in the entire circuit equal to 18,173 heat-units, but variously distributed between the battery-cell and the wire, according to the thickness of the latter. Now this quantity of heat is nearly the same as that which is evolved in the simple solution of 32·5 grams of zinc in dilute sulphuric acid, without the formation of a voltaic circuit, viz., 18,444 units. Hence Favre concludes that the heat developed by the resistance of a metallic or other conductor connecting the poles of the battery is simply borrowed from the total quantity of heat evolved by the chemical action taking place in the battery, and is rigorously complementary to that which remains in the cells of the battery, the heat evolved in the entire circuit being the exact equivalent of the chemical action which takes place. If any external work is performed by the current, such as electrolysis, or mechanical work, as by an electro-magnetic engine, the heat evolved in the circuit is diminished by the heat-equivalent of the decomposition or mechanical work done.

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* Ann. Ch. Phys. [3] xl. 393.

† Comptes Rendus, xlv. 56.

CHEMISTRY OF THE METALS.

THE metals constitute the second and larger group of elementary bodies. A great number of them are of very rare occurrence, being found only in a few scarce minerals; others are more abundant, and some few almost universally diffused throughout the globe. Some of these bodies are of most importance when in the metallic state; others, when in combination, chiefly as oxides, the metals themselves being almost unknown. Many are used in medicine and in the arts, and are essentially connected with the progress of civilisation.

If arsenic be included, the metals amount to fifty in number.

Physical Properties.—One of the most remarkable and striking characters possessed by the metals is their peculiar lustre: this is so characteristic, that the expression metallic *lustre* has passed into common speech. This property is no doubt connected with the great degree of opacity which the metals present in every instance. The thinnest leaves or plates, and the edges of crystalline laminæ, arrest the passage of light in the most complete manner. An exception to the rule is usually made in favour of gold-leaf, which, when held up to the day-light, exhibits a greenish, and in some cases a purple colour, as if it were really endued with a certain degree of translucency: the metallic film is, however, generally so imperfect that it is somewhat difficult to say whether the observed effect may not be in some measure due to multitudes of little holes, many of which are visible to the naked eye; but Faraday's experiments have established the translucency of gold beyond all doubt.

In point of *colour*, the metals present a certain degree of uniformity: with two exceptions—viz., copper, which is red, and gold, which is yellow—all these bodies are included between the pure white of silver and the bluish-grey tint of lead: bismuth, it is true, has a pinkish colour, and calcium and strontium, a yellowish tint, but these tints are very feeble.

The differences of *specific gravity* are very wide, passing from lithium, potassium, and sodium, which are lighter than water, to *platinum*, which is more than twenty-one times heavier than an equal bulk of that liquid.

Table of the Specific Gravities of Metals at 15·5° C. (60° F.)

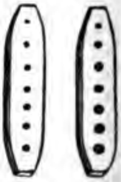
Platinum (in thin wire),	21·50
Gold,	19·50
Uranium,	18·40
Tungsten,	17·60
Mercury,	13·59
Palladium,	11·30 to 11·8
Lead,	11·45
Silver,	10·50
Bismuth,	9·90
Copper,	8·96
Nickel,	8·80
Cadmium,	8·70
Molybdenum,	8·63
Cobalt,	8·54
Manganese,	8·00
Iron,	7·79
Tin,	7·29
Zinc,	6·86 to 7·1
Antimony,	6·80
Arsenic,	5·88
Aluminium,	2·56 to 2·67
Magnesium,	1·75
Sodium,	0·972
Potassium,	0·865
Lithium,	0·593

The property of *malleability*, or power of extension under the hammer, or between the rollers of the flatting-mill, is possessed by certain of the metals to a very great extent. Gold-leaf is a remarkable example of the tenuity to which a malleable metal may be brought by suitable means. The gilding on silver wire used in the manufacture of gold lace is even thinner, and yet presents an unbroken surface. Silver may be beaten out very thin—copper also, but to an inferior extent; tin and platinum are easily rolled out into foil; iron, palladium, lead, nickel, cadmium, the metals of the alkalis, and mercury when solidified, are also malleable. Zinc may be placed midway between the malleable and brittle division; then perhaps bismuth; and, lastly, such metals as antimony and arsenic, which are altogether destitute of malleability.

The specific gravity of malleable metals is usually very sensibly increased by pressure or blows, and the metals themselves are rendered much harder, with a tendency to brittleness. This condition is destroyed and the former soft state restored by the operation of *annealing*, which consists in heating the metal to redness out of contact with air (if it will bear that temperature without fusion), and cooling it quickly, or slowly according to the circumstances of the case. After this operation, it is found to possess its original specific gravity.

Ductility is a property distinct from the last, inasmuch as it involves the principle of tenacity, or power of resisting tension. The art of wire-drawing is one of great antiquity; it consists in drawing rods of metal through a succession of trumpet-shaped holes in a steel plate, each being a little smaller than its predecessor, until the requisite degree of fineness is attained. The metal often becomes very hard and rigid in this process, and is then liable to break: this is remedied by annealing. The order of tenacity among the metals susceptible of being easily drawn into wire is the following: it is determined by observing the weights required to break asunder wires drawn through the same orifice of the plate:—

Fig. 141.



Iron.
Copper.
Platinum.
Silver.
Gold.
Zinc.
Tin.
Lead.

Metals differ as much in *fusibility* as in density. The following table will give an idea of their relations to heat:—

		Melting Points. F.	Melting Points. C.
Fusible below a red heat.	Mercury,	− 39°	− 39·44°
	Rubidium,	+ 101·3	+ 38·5
	Potassium,	144·5	62·5
	Sodium,	207·7	97·6
	Lithium,	356	180
	Tin,	442	227·8
	Cadmium, (about)	442	228
	Bismuth,	497	258
	Thallium,	561	294
	Lead,	617	325
	Tellurium,—rather less fusible than lead,		
	Arsenic,—unknown.		
	Zinc,	773	412
	Antimony,—just below redness.		
Infusible below a red heat	Silver,	1873	1023
	Copper,	1996	1091
	Gold,	2016	1102
	Cast-iron,	2786	1530
	Pure iron, Nickel, Cobalt, Manganese, Palladium,	Highest heat of Forge.	

Infusible below a red-heat.	Molybdenum,	Agglomerate, but do not melt in the forge.
	Uranium,	
	Tungsten,	
	Chromium,	
	Titanium,	Infusible in ordinary blast-furnaces; fusible by oxy-hydrogen blow-pipe.
	Cerium,	
	Osmium,	
	Iridium,	
	Rhodium,	
	Platinum,	
	Tantalum,	

Some metals acquire a pasty or adhesive state before becoming fluid: this is the case with iron and platinum, and with the metals of the alkalis. It is this peculiarity which confers the very valuable property of welding, by which pieces of iron and steel are united without solder, and the finely divided metallic sponge of platinum is converted into a solid and compact bar.

Some metals are *volatile*, and this character would perhaps be exhibited by all, could temperatures sufficiently elevated be obtained. Mercury boils and distils below a red heat; potassium, sodium, zinc, magnesium, and cadmium rise in vapour when heated to bright redness; arsenic and tellurium are volatile.

CHEMICAL RELATIONS OF THE METALS.

METALLIC combinations are of two kinds—namely, those formed by the union of metals among themselves, which are called alloys, or, where mercury is concerned, amalgams, and those generated by combination with the non-metallic elements, as oxides, chlorides, sulphides, &c. In this later case, the metallic characters are almost invariably lost.

Alloys.—Most metals are probably, to some extent, capable of existing in a state of combination with each other in definite proportions; but it is difficult to obtain these compounds in a separate state, since they dissolve in all proportions in the melted metals, and do not generally differ so widely in their melting points from the metals they may be mixed with, as to be separated by crystallisation in a definite form. Exceptions to this rule are met with in the cooling of argentiferous lead, and in the crystallisation of brass and of gun-metal.

The chemical force capable of being exerted between different metals is for the most part very feeble, and the consequent state of combination is therefore very easily disturbed by the influence of other forces. The stability of such metallic compounds is, however, greater in proportion to the general chemical dissimilarity of the metals they contain. But in all cases of combination between metals, the alteration of physical characters, which is the distinctive feature of chemical combination, does not take place to any great extent. The most unquestionable compounds of metals with metals are still metallic in their general physical characters, and there is no such transmutation of the individuality of their constituents as takes place in the combination of a metal with oxygen, sulphur, chlorine, &c. The alteration of characters in alloys is generally limited to the colour, degree of hardness, tenacity, &c., and it is only when the constituent metals are capable of assuming opposite chemical relations that these compounds are distinguished by great brittleness.

The formation of actual chemical compounds, in some cases, when two metals are melted together, is indicated by several phenomena, viz., the evolution of heat, as in the case of platinum and tin, copper and zinc, &c. The density of alloys differs from that of mere mixtures of the metals. In the solidification of alloys, the temperature does not always fall uniformly, but often remains stationary at particular degrees, which may be regarded as the solidifying points of the compounds then crystallising. Tin and lead melted together in any proportions always form a compound which solidifies at 187°. The melting point of an alloy is often very different from the point of solidification, and it is generally lower than the mean melting point of the constituent metals.

But though metals may combine when melted together, it is doubtful whether they remain combined after the solidification of the mass, and the wide differences between the melting and solidifying points of certain alloys appear to indicate that the existence of these compounds is limited to a certain range of temperature. Matthiessen* regards it as probable that the condition of an alloy of two metals in the liquid state may be either that of—1. A solution of one metal in another; 2. Chemical combination; 3. Mechanical mixture; or, 4. A solution or mixture of two or all of the above; and that similar differences may exist as to its condition in the solid state.

The chemical action of reagents upon alloys is sometimes very different from their action upon metals in the separate state: thus, platinum alloyed with silver is readily dissolved by nitric acid, but is not affected by that acid when unalloyed. On the contrary, silver, which in the separate state is readily dissolved by nitric acid, is not dissolved by it when alloyed with gold in proportions much less than one-fourth of the alloy by weight.

Compounds of Metals with Metalloids.—Classification of Metals.

A classification of the metals according to their quantivalence or atomicity is given in the table on p. 250; and each of the classes thus formed may be divided into groups, the individual members of which possess certain physical or chemical characters in common. There are, however, several metals, especially among those of rare occurrence, whose position in the series is by no means definitely fixed.

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* British Association Reports, 1863, p. 97.

CLASS I.—*Monad Metals.*—1. Among these metals, potassium, sodium, cæsium, rubidium, and lithium, are called *alkali-metals.* They are soft, easily fusible, volatile at higher temperatures; combine very energetically with oxygen; decompose water at all temperatures; and form strongly basic oxides, which are very soluble in water, yielding powerfully caustic and alkaline hydroxides, not decomposable by heat. Their carbonates are soluble in water, and each metal forms only one chloride. The hypothetical metal ammonium, NH_4 (p. 164), is usually added to the list of alkali-metals, on account of the general similarity of its compounds to those of potassium and sodium.

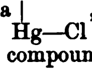
2. Silver differs greatly from the alkali-metals in its physical and most of its chemical properties, but it is related to them by the isomorphism of some of its compounds with the corresponding compounds of those metals; thus it forms an alum, similar in form and composition to ordinary potash alum.

CLASS II.—*Dyad Metals.*—1. The three metals, barium, strontium, and calcium, form oxides called *alkaline earths,* less soluble in water than the true alkalis, but exhibiting similar taste, causticity, and action on vegetable colours. The metals of this group form but one chloride, *e.g.*, $BaCl_2$; their carbonates are insoluble in water, and barium sulphate is also insoluble, strontium and calcium sulphates slightly soluble.

2. A second group consists of the metals beryllium, yttrium, erbium, lanthanum, and didymium, which form oxides called *earths,* insoluble in water, and not reducible to the metallic state by hydrogen or carbon; their carbonates are insoluble in water, their sulphates soluble. These metals also form but one chloride, viz., a dichloride. They are all very rare. Mendelejeff, as already observed (p. 266), proposes to classify didymium, yttrium, and erbium as triads, and lanthanum as a tetrad; but his reasons for doing so are not very conclusive: at all events it is most convenient to describe these metals amongst the earth-metals.

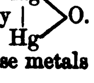
3. Magnesium, zinc, and cadmium resemble one another in being volatile at high temperatures, and burning when heated in the air; they decompose water at high temperatures, eliminate hydrogen from dilute acids, and form only one oxide and one chloride, *e.g.*, ZnO and $ZnCl_2$. Magnesium was formerly classed as an earth-metal, but it bears a much closer analogy to zinc.

4. Mercury and copper each form two chlorides and two oxides: mercury, for example, forms the two chlorides, $HgCl_2$ and Hg_2Cl_2, and the two oxides, HgO and Hg_2O. Mercurous chloride (calomel) is represented by the formula



$$\begin{array}{l}Hg{-}Cl\\ |\\ Hg{-}Cl\end{array}$$

, and the corresponding oxide by



$$\begin{array}{l}Hg\diagdown\\ |\quad\;\; >O\\ Hg\diagup\end{array}$$

. The copper compounds are similarly constituted. These metals do not decompose water at any temperature; they are oxidised by nitric and by strong sulphuric acids. The oxides of mercury are reduced to the metallic state by heat alone; those of copper by ignition with hydrogen or charcoal.

The position of copper in the series has already been discussed (p. 265). It has certain analogies with the metals of the iron group—and in the cuprous compounds it may be regarded as univalent; but in its most stable compounds, the cupric salts, it is unquestionably bivalent.

CLASS III.—*Triad Metals.*—The metals referable to this class are aluminium, gallium, indium, thallium, and gold. The first three form only trichlorides; thallium and gold form monochlorides and trichlorides, also corresponding oxides, *e.g.*, thallium chlorides, TlCl and $TlCl_3$; oxides, Tl_2O and Tl_2O_3. The mono-compounds of thallium are much more stable than the tri-compounds, and in respect of these compounds thallium exhibits very close analogies to the alkali-metals, forming, for example, an alum isomorphous with common potash alum, and phosphates analogous in composition to the phosphates of sodium. The position of gold has already been discussed. Aluminium is sometimes regarded as a tetrad, but for reasons already given (p. 265) it is most probably a triad.

CLASS IV.—*Tetrad Metals.*—To this class belong zirconium, thorinum, cerium, tin, titanium, and lead. Zirconium and thorinum form tetrachlorides and dioxides. The position of cerium in the series is altogether doubtful.

Tin and titanium are closely related to silicium, each forming a volatile tetrachloride; namely, stannic chloride, $SnCl_4$, and titanic chloride, $TiCl_4$, together with the corresponding oxides. Tin likewise forms the stannous compounds in which it is bivalent, *e.g.*, $SnCl_2$, SnO; and titanium forms the titanous compounds, in which it is apparently trivalent but really quadrivalent: *e.g.*, $TiCl_3$ or $Ti_2Cl_6 = Cl_3Ti-TiCl_3$.

The quadrivalence of lead is inferred from the composition of *plumbo-tetrethide*, $Pb(C_2H_5)_4$; but in most of its compounds it is bivalent, forming only one chloride, $PbCl_2$, with corresponding iodide, bromide, and fluoride. It forms also the corresponding oxide, PbO, together with a lower oxide, Pb_2O, and three higher oxides, Pb_3O_4, Pb_4O_5, and PbO_2. Lead is allied to barium and strontium by the isomorphism of its sulphate with the sulphates of barium and strontium, and to silver, thallium, and mercury by the sparing solubility of its chloride, which is precipitated by hydrochloric acid from solutions of lead salts.

Platinum and its allied metals also form tetrachlorides and dioxides; but these metals are best regarded as forming a group by themselves.

CLASS V.—*Pentad Metals.*—1. Arsenic forms a trichloride, a trioxide, and corresponding salts; also a pentoxide, and corresponding salts, called arsenates, analogous to the phosphates. Antimony forms a trichloride and a pentachloride analogous to those of phosphorus, also the corresponding oxides. Bismuth forms a volatile trichloride, and a dichloride, Bi_2Cl_4, or $\begin{array}{c}\mathrm{BiCl_2}\\ |\\ \mathrm{BiCl_2}\end{array}$. Vanadium was formerly supposed to belong to the tungsten group, but it has lately been shown to be a pentad. It forms a trichloride, VCl_3; also an oxychloride, $VOCl_3$, analogous to phosphorus oxychloride; and the oxides, V_2O_3 and V_2O_5, analogous to those of phosphorus and arsenic, the latter yielding a series of salts, the vanadates, isomorphous with the phosphates and arsenates of corresponding composition.

2. Tantalum and niobium, formerly regarded as tetrads, have been shown by Marignac to form pentachlorides and pentoxides. The oxides of the pentad metals are, for the most part, of acid character.

Class VI.—*Hexad Metals.*—1. Chromium forms a hexfluoride, CrF_6, and a corresponding oxide, CrO_3. It likewise forms two series of compounds, in which it exhibits lower degrees of equivalence, viz., the chromic compounds analogous to the ferric compounds, in which, like aluminium and iron, it is either trivalent or quadrivalent; *e.g.*, chromic chloride, $CrCl_3$ or $Cr_2Cl_6 = \begin{array}{c}\mathrm{CrCl_3}\\ |\\ \mathrm{CrCl_3}\end{array}$; and the chromous compounds, analogous to the ferrous compounds, in which it is bivalent, *e.g.*, $CrCl_2$, CrO.

Uranium forms a trioxide, UO_3, and an oxychloride, UO_2Cl_2, analogous to CrO_2Cl_2.

2. Tungsten forms a hexchloride, WCl_6, and the corresponding oxide, WO_3. Molybdenum is not known to form a chloride higher than $MoCl_4$, but its trioxide, MoO_3, is known; and from the general similarity of the tungsten and molybdenum compounds, the latter metal is inferred to be hexadic.

Class VII.—*Heptad Metals.*—The only metal at present referable to this class is Manganese, which forms a heptachloride, and may also be regarded as heptadic in permanganic acid, $HMnO_4$, and its salts, which, as already observed, are isomorphous with the perchlorates (p. 267). Manganese is, however, more conveniently described in connection with the iron group of metals.

Class VIII.—*Iron* and *Platinum Metals.*—These metals, for reasons already assigned, cannot be referred to either of the preceding classes (p. 268). Besides possessing certain physical properties in common, they exhibit a greater tendency than any of the preceding to enter into combination, sometimes as perissads, sometimes as artiads.

The nine metals of this class resemble one another in many respects:—(1.) They are all of grey colour and difficult of fusion.

(2.) They possess in a high degree the power of condensing and giving passage to gases, as seen especially in nickel, palladium, iron, and platinum. (3.) Their highest oxides are bases, or acids of little energy, which are easily reduced to lower oxides of more decided basic character. (4.) They form stable double cyanides with the alkali-metals, Fe, Ru, and Os, yielding analogous compounds having the general formula K_4RCy_6; Co, Rh, Ir forming salts having the general formula K_3RCy_6; Ni, Pd, Pt forming salts having the composition K_2RCy_4. (8.) Some of their compounds, especially those of the higher degrees of combination, are distinguished by characteristic colours.

Copper and gold might, on account of analogous behaviour, be included in the eighth class; although, according to the constitution of their lower oxides, they belong to the first or monadic class.

The *Iron Group* includes iron, nickel, and cobalt, perhaps also manganese, chromium, and cerium. Iron in the ferrous compounds is bivalent; in the ferric compounds it may be regarded either as trivalent or as quadrivalent, ferric chloride, for example, being either $FeCl_3$ or $Fe_2Cl_6 = Cl_3Fe-FeCl_3$. The vapour-density of the compound tends rather to support the latter formula. Iron also forms salts called ferrates, analogous to the chromates, in which it is sexvalent. Cobalt forms two series of compounds analogous to the ferrous and ferric compounds; nickel is for the most part bivalent, but it also forms a sesquioxide Ni_2O_3.

Manganese, as above mentioned, is septivalent in its highest chloride, $MnCl_7$ (the composition of which is, however, somewhat doubtful) and in the permanganates; in its other compounds it resembles iron, being bivalent in the manganous, tri- or quadrivalent in the manganic compounds, and sexvalent in the manganates, *e.g.*, K_2MnO_4, which are analogous to the sulphates, chromates, and ferrates. All these metals decompose water at high temperatures. Nickel and cobalt are magnetic like iron, and their salts are isomorphous with the corresponding iron compounds.

Chromium forms three series of compounds analogous in composition and in many of their properties to the ferrous and ferric salts and the ferrates. Chromic acid, however, and the corresponding anhydride are very stable compounds; whereas ferric acid and the corresponding anhydrous oxide, FeO_3, are unknown, and the ferrates are very unstable. Cerium is bivalent in the cerous salts, sexvalent in ceric fluoride, CeF_6, and forms an oxide, Ce_3O_4, analogous to ferroso-ferric oxide, Fe_3O_4, and corresponding salts.

Platinum Metals.—Platinum, palladium, iridium, rhodium, ruthenium, and osmium, form a natural group of metals, occurring together in the metallic state, and resembling each other in many of their properties. Platinum and palladium form dichlorides and tetrachlorides, with corresponding oxides, viz., $PtCl_2$, $PtCl_4$, PtO, PtO_2. Iridium forms a dichloride, a tetrachloride, and an intermediate chloride, which may be regarded either as $IrCl_3$ or as $Ir_2Cl_6 = Cl_3Ir - IrCl_3$. Ruthenium and osmium form chlorides similar in constitution to those of iridium; rhodium only a dichloride, $RhCl_2$, and a trichloride, Rh_2Cl_6. All these metals form oxides analogous in composition to their chlorides, *e.g.*, IrO, Ir_2O_3, IrO_2, and likewise higher oxides, iridium and rhodium forming trioxides, IrO_3 and RhO_3, and osmium and ruthenium forming tetroxides, OsO_4 and RuO_4; but there are no chlorides corresponding with these oxides. The metals of the platinum group are not acted upon by nitric acid, but only by chlorine or nitromuriatic acid. With the exception of osmium, they do not oxidise in the air at any temperature, and their oxides are all reducible by heat alone. These metals, together with gold, silver, and mercury, which likewise exhibit the last-mentioned character, are sometimes called *noble metals.*

The metals of the alkalis and alkaline earths, on account of their inferior specific gravity, are often called light metals; the others, heavy metals.

Metallic Chlorides.—All metals combine with chlorine, and most of them in several proportions, as above indicated, forming compounds which may be regarded as derived from one or more molecules of hydrochloric acid, by substitution of a metal for an equivalent quantity of hydrogen; thus:—

From	HCl	are derived	monochlorides	like	KCl
,,	H_2Cl_2	,,	dichlorides	,,	$BaCl_2$
,,	H_3Cl_3	,,	trichlorides	,,	$AuCl_3$
,,	H_4Cl_4	,,	tetrachlorides	,,	$SnCl_4$, &c., &c.

Hydrochloric acid may, in fact, be regarded as the type of chlorides in general.

Several chlorides occur as natural products. Sodium chloride, or common salt, occurs in enormous quantities, both in the solid state as rock-salt, and dissolved in sea-water, and in the water of rivers and springs. Potassium chloride occurs in the same forms, but in smaller quantity; the chlorides of lithium, cæsium, rubidium, and thallium also occur in small quantities in certain spring waters. Mercurous chloride, Hg_2Cl_2, and silver chloride, $AgCl$, occur as natural minerals.

1. Chlorides are generally prepared by one or other of the following processes: (1.) By acting upon the metal with chlorine gas. Antimony pentachloride and copper dichloride are examples of chlorides sometimes produced in this manner. The chlorides of

gold and platinum are usually prepared by acting upon the metals with nascent chlorine, developed by hydrochloric and nitric acids. Sometimes, on the other hand, the metal is in the nascent state, as when titanic chloride is formed by passing a current of chlorine over a heated mixture of charcoal and titanic oxide. The chlorides of aluminium and chromium may be obtained by similar processes.

2. Chlorine gas, by its action upon metallic oxides, drives out the oxygen, and unites with the respective metals to form chlorides. This reaction sometimes takes place at ordinary temperatures, as in the case with silver oxide; sometimes only at a red heat, as is the case with the oxides of the alkali-metals, and alkaline earth-metals. The hydroxides and carbonates of these last metals, when dissolved or suspended in hot water and treated with excess of chlorine, are converted, chiefly into chlorides, partly into chlorates.

3. Many metallic chlorides are prepared by acting upon the metals with hydrochloric acid. Zinc, cadmium, iron, nickel, cobalt, and tin dissolve readily in hydrochloric acid, with liberation of hydrogen; copper only in the strong boiling acid; silver, mercury, palladium, platinum, and gold, not at all. Sometimes the metal is substituted, not for hydrogen, but for some other metal. Stannous chloride, for instance, is frequently made by distilling metallic tin with mercuric chloride; thus: $HgCl_2 + Sn = SnCl_2 + Hg$.

4. By dissolving a metallic oxide, hydroxide, or carbonate in hydrochloric acid.

All monochlorides and dichlorides are soluble in water, excepting silver chloride, $AgCl$, and mercurous chloride, Hg_2Cl_2; lead chloride, $PbCl_2$, is sparingly soluble; these three chlorides are easily formed by precipitation. Many metallic chlorides dissolve also in alcohol and in ether.

Most monochlorides, dichlorides, and trichlorides volatilise at high temperatures without decomposition; the higher chlorides when heated give off part of their chlorine. Some chlorides which resist the action of heat alone are decomposed by ignition in the air, yielding metallic oxides and free chlorine: this is the case with the dichlorides of iron and manganese; but most dichlorides remain undecomposed, even in this case. All metallic chlorides, excepting those of the alkali-metals and earth-metals, are decomposed at a red heat by hydrogen gas, with formation of hydrochloric acid: in this way metallic iron may be obtained in fine cubical crystals. Silver chloride, placed in contact with metallic zinc or iron, under dilute sulphuric or hydrochloric acid, is reduced to the metallic state by the nascent hydrogen.

Sulphuric, phosphoric, boric, and arsenic acids decompose most metallic chlorides, sometimes at ordinary, sometimes at higher temperatures. All metallic chlorides, heated with lead dioxide or manganese dioxide and sulphuric acid, give off chlorine, *e.g.*:

$$\underset{\substack{\text{Sodium}\\\text{chloride.}}}{2NaCl} + \underset{\substack{\text{Manganese}\\\text{dioxide.}}}{MnO_2} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{2H_2SO_4} = \underset{\substack{\text{Sodium}\\\text{sulphate.}}}{Na_2SO_4} + \underset{\substack{\text{Manganous}\\\text{sulphate.}}}{MnSO_4} + 2H_2O + Cl_2.$$

Chlorides distilled with sulphuric acid and potassium chromate, yield a dark bluish-red distillate of chromic oxychloride. Some metallic chlorides are decomposed by *water*, forming hydrochloric acid and an oxychloride, *e.g.*: $BiCl_3+H_2O=2HCl+BiClO$. The chlorides of antimony and stannous chloride are decomposed in a similar manner.

All soluble chlorides give with solution of *silver nitrate*, a white precipitate of silver chloride, easily soluble in ammonia, insoluble in nitric acid. With *mercurous nitrate*, they yield a white curdy precipitate of mercurous chloride, blackened by ammonia; and with *lead-salts*, not too dilute, a white precipitate of lead chloride, soluble in excess of water.

Metallic chlorides unite with each other and with the chlorides of the non-metallic elements, forming such compounds as potassium chloromercurate, $2KCl.HgCl_2$, sodium chloroplatinate, $2NaCl.PtCl_4$, potassium chloriodate, $KCl.ICl_3$, &c. Metallic chlorides combine in definite proportions with ammonia and organic bases: the chlorides of platinum form with ammonia the compounds $2NH_3.PtCl_2$, $4NH_3.PtCl_2$, $2NH_3.PtCl_4$, and $4NH_3.PtCl_4$; mercuric chloride forms with aniline the compound $2C_6H_7N.HgCl_2$, &c.

Chlorides also unite with oxides and sulphides, forming *oxychlorides* and *sulphochlorides*, which may be regarded as chlorides having part of their chlorine replaced by an equivalent quantity of oxygen or sulphur (Cl_2 by O or S). Bismuth, for example, forms an oxychloride having the composition $BiClO$ or $BiCl_3.Bi_2O_3$.

Bromides.—Bromine unites directly with most metals, forming compounds analogous in composition to the chlorides, and resembling them in most of their properties. The bromides of the alkali-metals occur in sea-water and in many saline springs; silver bromide occurs as a natural mineral. Nearly all bromides are soluble in water, and may be formed by treating an oxide, hydroxide, or carbonate, with hydrobromic acid, the solutions when evaporated giving off water for the most part, and leaving a solid metallic bromide; some of them, however, namely, the bromides of magnesium, aluminium, and the other earth-metals, are more or less decomposed by evaporation, giving off hydrobromic acid, and leaving a mixture of metallic bromide and oxide. Silver bromide and mercurous bromide are insoluble in water, and lead bromide is very sparingly soluble; these are obtained by precipitation.

Metallic bromides are solid at ordinary temperatures; most of them fuse at a moderate heat, and volatilise at higher temperatures. The bromides of gold and platinum are decomposed by mere exposure to heat; many others give up their bromine when heated in contact with the air. *Chlorine*, with the aid of heat, drives out the bromine and converts them into chlorides. *Hydrochloric acid* also decomposes them at a red heat, giving off hydrobromic acid. Strong *sulphuric* or *nitric acid* decomposes them, with evolution of hydrobromic acid, which, if the sulphuric or nitric acid is concentrated, and in excess, is partly decomposed, with separation of bromine and formation of sulphurous oxide or nitrogen dioxide. Bromides heated with *sulphuric acid* and *manganese dioxide* or *potassium chromate*, give off free bromine.

Bromides in solution are easily decomposed by chlorine, either in the form of gas or dissolved in water, the liquid acquiring a red or reddish-yellow colour, according to the quantity of bromine present; and on agitating the liquid with ether, that liquid dissolves the bromine, forming a red solution, which rises to the surface.

Soluble bromides give with *silver nitrate* a white precipitate of silver bromide, greatly resembling the chloride, but much less soluble in ammonia, insoluble in hot nitric acid. *Mercurous nitrate* produces a yellowish-white precipitate; and *lead acetate*, a white precipitate much less soluble in water than the chloride. *Palladium nitrate* produces in solutions of bromides not containing chlorine, a black precipitate of bromide. Palladium chloride produces no precipitate; neither does the nitrate, if soluble chlorides are present.

Bromides unite with each other in the same manner as chlorides; also with oxides, sulphides, and ammonia.

Iodides.—These compounds are obtained by processes similar to those which yield the chlorides and bromides. Many metals unite directly with iodine. Potassium and sodium iodides exist in sea-water and in many salt-springs; silver iodide occurs as a natural mineral.

Metallic iodides are analogous to the bromides and chlorides in composition and properties. But few of them are decomposed by heat alone; the iodides of gold, silver, platinum, and palladium, however, give up their iodine when heated.

Most metallic iodides are perfectly soluble in water; but lead iodide is very slightly soluble, and the iodides of mercury and silver are quite insoluble.

Solutions of iodides evaporated out of contact of air, generally leave anhydrous metallic iodides, which partly separate in the crystalline form before the water is wholly driven off. The iodides of the earth-metals, however, are resolved, on evaporation, into the earthy oxides and hydriodic acid, which escapes. A very small quantity of *chlorine* colours the solution yellow or brown, by partial decomposition; and a somewhat larger quantity takes up the whole of the metal, forming a chloride, and separates the iodine, which then gives a blue colour with starch; a still larger quantity of chlorine gives the liquid a paler colour, and converts the separated iodine into trichloride of iodine, which does not give a blue colour with starch, and frequently enters into combination with the metallic chloride produced. Strong *sulphuric acid* and somewhat concentrated *nitric acid* colour the solution yellow or brown; and if the quantity of the iodide is large, and the solution much concentrated or heated, they liberate iodine, which partly escapes in violet vapours. *Starch mixed with* the solution, even if it be very dilute, is turned blue—

permanently when the decomposition is effected by sulphuric acid; for a time only when it is effected by nitric acid, especially if that acid be added in large quantity.

The aqueous solution of an iodide gives a brown precipitate with salts of *bismuth;* orange-yellow with *lead* salts; dirty-white with *cuprous* salts, and also with *cupric* salts, especially on the addition of sulphurous acid; greenish-yellow with *mercurous* salts; scarlet with *mercuric* salts; yellowish-white with *silver* salts; lemon-yellow with *gold* salts; brown with *platinic* salts—first, however, turning the liquid dark brown red; and black with salts of *palladium*, even when extremely dilute. All these precipitates consist of metallic iodides, many of them soluble in excess of the soluble iodide: the silver precipitate is insoluble in nitric acid and very little soluble in ammonia.

Metallic iodides unite with one another, forming double iodides, analogous to the double chlorides; they also absorb ammonia gas in definite proportions. Some of them, as those of antimony and tellurium, unite with the oxides of the corresponding metals, forming oxyiodides.

Fluorides.—These compounds are formed—1. By heating hydrofluoric acid with certain metals. 2. By the action of that acid on metallic oxides. 3. By heating electro-negative metals—antimony, for example—with fluoride of lead or fluoride of mercury. 4. Volatile metallic fluorides may be prepared by heating fluor-spar with sulphuric acid and the oxide of the metal.

Fluorides have no metallic lustre; most of them are easily fusible, and for the most part resemble the chlorides. They are not decomposed by ignition, either alone or when mixed with charcoal. When ignited in contact with the air, in a flame which contains aqueous vapour, many of them are converted into oxides, while the fluorine is given off as hydrofluoric acid. All fluorides are decomposed by *chlorine*, and converted into chlorides. They are not decomposed by *phosphoric oxide*, unless silica is present. They are decomposed at a gentle heat by strong *sulphuric acid*, with formation of a metallic sulphate and evolution of hydrofluoric acid.

The fluorides of tin and silver are easily soluble in water; those of potassium, sodium, and iron are sparingly soluble; those of strontium and cadmium very slightly soluble, and the rest insoluble. The solutions of ammonium, potassium, and sodium fluoride have an alkaline reaction. The aqueous solutions of fluorides corrode glass vessels in which they are kept or evaporated. They form with soluble *calcium-salts* a precipitate of calcium fluoride, in the form of a transparent jelly, which is scarcely visible, because its refractive power is nearly the same as that of the liquid; the addition of ammonia makes it plainer. This precipitate, if it does not contain silica, dissolves with difficulty in hydrochloric or nitric acid, and is re-precipitated by ammonia. The aqueous fluorides give a pulverulent precipitate with lead acetate.

The fluorides of antimony, arsenic, chromium, mercury, niobium, osmium, tantalum, tin, titanium, tungsten, and zinc, are volatile without decomposition.

Fluorine has a great tendency to form double salts, consisting of a fluoride of a basic or positive metal united with the fluoride of hydrogen, boron, silicon, tin, titanium, zirconium, &c., *e.g.*—

Potassium hydrofluoride,	KHF_2	$= KF.HF$
Potassium borofluoride	KBF_4	$= KF.BF_3$
Potassium silicofluoride,	K_2SiF_6	$= 2KF.SiF_4$
Potassium titanofluoride,	K_2TiF_6	$= 2KF.TiF_4$
Potassium stannofluoride,	K_2SnF_6	$= 2KF.SnF_4$
Potassium zircofluoride,	K_2ZrF_6	$= 2KF.ZrF_4$.

The four classes of compounds just described, the chlorides, bromides, iodides, and fluorides, form a group often designated as **haloïd compounds** or **haloïd* salts**, from their analogy to sodium chloride or sea salt, which may be regarded as a type of them all The elements, chlorine, bromine, iodine, and fluorine, are called halogens.

Cyanides.—Closely related to these haloïd compounds are the cyanides, formed by the union of metals with the group CN, cyanogen, which is a monatomic radicle derived from the saturated molecule, $C{\equiv}N{-}H$ (hydrocyanic acid), by abstraction of H; in short, the cyanides may be regarded as chlorides having the element Cl replaced by the compound radicle CN (p. 186).

Some metals—potassium among the number—are converted into cyanides by heating them in cyanogen gas or vapour of hydrocyanic acid. The cyanides of the alkali-metals are also formed (together with cyanates) by passing cyanogen gas over the heated hydroxides or carbonates of the same metals; potassium cyanide also, by passing nitrogen gas over a mixture of charcoal and hydroxide or carbonate of potassium at a bright red heat. Cyanides are formed abundantly when nitrogenous organic compounds are heated with fixed alkalis. Other modes of formation will be mentioned hereafter.

The cyanides of the alkali-metals and of barium, strontium, calcium, magnesium, and mercury, are soluble in water, and may be produced by treating the corresponding oxides or hydroxides with hydrocyanic acid. Nearly all other metallic cyanides are insoluble, and are obtained by precipitation from the soluble cyanides.

The cyanides of the alkali-metals sustain a red heat without decomposition, provided air and moisture be excluded. The cyanides of many of the heavy metals, as lead, iron, cobalt, nickel, and copper, under these circumstances, give off all their nitrogen as gas, and leave a metallic carbonate; mercuric cyanide is resolved into mercury and cyanogen gas; silver cyanide gives off half its cyanogen as gas. Most cyanides, when heated with dilute acids, give off their cyanogen as hydrocyanic acid.

---

* From ἅλς, the sea.

Cyanides have a strong tendency to unite with one another, forming **double cyanides.** The most important of these are the double cyanides of iron and potassium, namely, *potassio-ferrous cyanide*, $Fe''K_4(CN)_6$, commonly called yellow prussiate of potash; and *potassio-ferric cyanide*, $Fe'''K_3(CN)_6$, commonly called red prussiate of potash. Both these are splendidly crystalline salts, which dissolve easily in water, and form highly characteristic precipitates with many metallic salts. These salts, with the other cyanides, will be more fully described under "Organic Chemistry;" but they are mentioned here, on account of their frequent use in the qualitative analysis of metallic solutions.

Oxides.—All metals combine with oxygen, and most of them in several proportions. In almost all cases oxides are formed corresponding in composition with the chlorides, one atom of oxygen taking the place of two atoms of chlorine. Many metals also form oxides to which no chlorine analogues are known; thus lead, which forms only one chloride, $PbCl_2$, forms, in addition to the monoxide, PbO, a dioxide, PbO_2, besides oxides of intermediate composition; osmium also, the highest chloride of which is $OsCl_4$, forms, in addition to the dioxide, a trioxide and a tetroxide. This arises from the fact that any number of atoms of oxygen or other dyad element may enter into a compound without disturbing the balance of equivalency (p. 262).

Just as chlorides are derived by substitution from hydrochloric acid, HCl (p. 311), so likewise may oxides be derived from one or more molecules of water, H_2O; but as the molecule of water contains two hydrogen-atoms, the replacement of the hydrogen may, as already explained (p. 245), be either total or partial, the product in the first case being an anhydrous metallic oxide, and in the second a hydrated oxide or hydroxide, in which the oxygen is associated both with hydrogen and with metal; in this manner the following hydroxides and anhydrous oxides may be constituted:

Type.	Hydroxides.	Oxides.
H_2O	KHO	K_2O $Ba''O$
H_4O_2	$Ba''H_2O_2$ $Bi'''HO_2$	$Sn^{iv}O_2$
H_6O_3	$As^{v}HO_3$ $Sn^{iv}H_2O_3$	Sb'''_2O_3 $W^{vi}O_3$
H_8O_4	$Zr^{iv}H_4O_4$	
$H_{10}O_5$		$Sb^{v}_2O_5$.

It may be observed that the hydroxides of artiad metals contain the elements of a molecule of the corresponding anhydrous oxide, and of one or more molecules of water, and may therefore also be regarded as hydrates; thus—

Barium hydroxide or hydrate,	$Ba''H_2O_2 = Ba''O.H_2O$
Stannic " "	$Sn^{iv}H_2O_3 = Sn^{iv}O_2.H_2O$
Zirconium " "	$Zr^{iv}H_4O_4 = Zr^{iv}O_2.2H_2O$.

as hydrates, that is, as compounds of anhydrous

Many metallic oxides occur as natural m
especially those of iron, tin, and copper, in large
ores from which the metals are extracted.

All metals, except gold, platinum, iridium, rh
ium, are capable of uniting directly with oxygen.
sodium, and barium, oxidise rapidly on expo
ordinary temperatures, and decompose water
metals, however, when in the massive state, rem
and unacted on in dry air or oxygen gas, but o
moisture is present; such is the case with iron, zi
of the ordinarily permanent metals, when in a
state, as lead when obtained by ignition of it
reduced from its oxide by ignition in hydrogen
oxidise spontaneously as soon as they come in c
Lead, iron, copper, and the volatile metals, arse
cadmium, and mercury, are converted into oxi
air or oxygen. Many metals, especially at a re
oxidised by water or steam. A very general m
metallic oxides is to subject the corresponding hyd
nitrates, sulphates, or any oxygen-salts containi
the action of heat.

Oxides are for the most part opaque earthy
metallic lustre. The majority of them are fusible
bismuth at a low red heat; those of copper and ir
those of barium and aluminium before the oxy-hy
while calcium oxide or lime does not fuse at any te
it has yet been subjected.

The superior oxides of the metals are easily reduced to a lower state of oxidation by treatment with a current of *hydrogen gas* at a more or less elevated temperature. At a higher degree of heat, hydrogen gas will transform to the reguline state all metallic oxides except the sesquioxides of aluminium and chromium, and the monoxides of manganese, magnesium, barium, strontium, calcium, lithium, sodium, and potassium. The temperature necessary to enable hydrogen to effect the decomposition of some oxides is comparatively low. Thus metallic iron may be reduced from its oxides by hydrogen gas at a heat considerably below redness. *Carbon*, at a red or white heat, is a still more powerful deoxidating agent than hydrogen, and seems to be capable of completely reducing all metallic oxides whatsoever. The oxidisable metals in general act as reducing agents.

Chlorine decomposes all metallic oxides, except those of the earth-metals, converting them into chlorides, and expelling the oxygen. With silver oxide this reaction takes place at ordinary temperatures; with the alkalis and alkaline earths, at a full red heat. *Sulphur*, at high temperatures, can decompose most metallic oxides; with many oxides—those of silver, mercury, lead, and copper, for instance—metallic sulphides and sulphur dioxide are produced; with the highly basylous oxides, the products are metallic sulphate and sulphide. There are some oxides upon which sulphur exerts no action. Of these the principal are magnesia, alumina, chromic, stannic, and titanic oxides. By boiling sulphur with soluble hydroxides, mixtures of polysulphide and thiosulphate are produced. With the exception of magnesia, alumina, and chromic oxide, most metallic oxides can absorb sulphuretted hydrogen, to form metallic sulphide or hydrosulphide and water.

Oxygen-salts or **Oxysalts.**—It has been already explained in the chapter on Oxygen (p. 123) that oxides may be divided into three classes, *acid*, *neutral*, and *basic*; the first and third being capable of uniting with one another in definite proportions, and forming compounds called salts. The most characteristic of the acid oxides are those of certain metalloids, as nitrogen, sulphur, and phosphorus, which unite readily with water or the elements of water, forming compounds called oxygen-acids, distinguished by sour taste, solubility in water, and the power of reddening certain vegetable blue colours. The most characteristic of the basic oxides, on the other hand, are those of the alkali-metals and alkaline earth-metals (p. 307), which likewise dissolve in water, but form alkaline solutions, possessing in an eminent degree the power of *neutralising* acids and forming salts with them. The same power is exhibited more or less by the monoxides of most other metals, as zinc, iron, copper, manganese, &c., and by the sesquioxides of aluminium, iron, chromium, and others. The higher oxides of several of these metals—the trioxides of chromium, for example—exhibit acid characters, being capable of forming salts with the more basic and form salts.

But in the majority of cases metallic salts are tion, or interchange of a metal for hydrogen, another. It is clear, indeed, that any metallic $ZnO.SO_3$, for example) may be derived from the c hydrogen salt ($H_2O.SO_3$) by substitution of a met quantity of hydrogen. Accordingly, metallic s produced by the action of an acid on a metal or hydroxide, thus—

(1.)	H_2SO_4 Hydrogen sulphate.	+	Zn	=	ZnS Zinc sulpha
(2.)	$2HNO_3$ Hydrogen nitrate.	+	Ag_2O Silver oxide.	=	$2AgN$ Silve nitrat
(3.)	HNO_3 Hydrogen nitrate.	+	KHO Potassium hydroxide.	=	KN Potassi nitrat

In the instances represented by these equation formed are soluble in water. Insoluble salts are by interchange of the metals between two solubl

(4.)	$Ba(NO_3)_2$ Barium nitrate.	+	Na_2SO_4 Sodium sulphate.	=	BaS Bariu sulph

In this case the barium sulphate, being insolu while the sodium nitrate remains in solution.

In all these reactions, hydrochloric acid or might be substituted for the oxygen-acid or oxyg analogous in composition to chlorides,—that is to say, as compounds of a metal with a radicle or group of elements, such as NO_3 (*nitrione*) in the nitrates, SO_4 (*sulphione*), in the sulphates, discharging functions similar to those of chlorine, and capable, like that element, of passing unchanged from one compound to another.

For many years, indeed, it was a subject of discussion among chemists, whether the former or the latter of these views should be regarded as representing the *actual* constitution of oxygen-salts. Berzelius divided salts into two classes:—1. Haloïd salts, comprising, as already mentioned, the chlorides, bromides, iodides, and fluorides, which are compounds of a metal with a monad metallic element.—2. Amphid salts, consisting of an acid or electro-negative oxide, sulphide, selenide, or telluride, with a basic or electro-positive compound of the same kind; such as potassium arsenate, $3K_2O.As_2O_5$; potassium sulpharsenate, $3K_2S.As_2S_5$; potassium seleniophosphate, $2K_2Se.P_2Se_5$, &c.

Davy, on the other hand, observing the close analogy between the reactions of chlorides, on the one hand, and of oxygen-salts, such as sulphates, nitrates, &c., on the other, suggested that the latter might be regarded, like the former, as compounds of metals with acid or electro-negative radicles, the only difference being, that in the former the acid radicle is an elementary body, Cl, Br, &c., whereas in the former it is a compound, as SO_4, NO_3, PO_4, &c. This was called the *binary theory of salts;* it was supported by many ingenious arguments by its proposer and several contemporary chemists; in later years also by Liebig, and by Daniell and Miller, who observed that the mode of decomposition of salts by the electric current is more easily represented by this theory than by the older one (p. 290.)

At the present day, the relative merits of these two theories are not regarded as a point of very great importance. Chemists, in fact, no longer attempt to construct formulæ which shall represent the actual arrangement of atoms in a compound, the formulæ now in use being rather intended to exhibit, first, the balance or neutralisation of the units of equivalency or atomicity of the several elements contained in a compound (p. 257); and, secondly, the manner in which any compound or group of atoms splits up into subordinate groups under the influence of different reagents. According to the latter view, a compound containing three or more elementary atoms may be represented by different formulæ corresponding with the several ways in which it decomposes. Thus hydrogen sulphate or sulphuric acid, H_2SO_4, may be represented by either of the following formulæ:—

1. $H_2.SO_4$, which represents the separation of hydrogen and formation of a metallic sulphate, by the action of zinc, &c.; this is the formula corresponding with the binary theory of salts.

2. $SO_3.H_2O$. This formula represents the formation of the acid by direct hydration of sulphuric oxide; the separation of water and formation of a metallic sulphate by the action of magnesia and other

anhydrous oxides; and the separation of sulphuric oxide and formation of phosphoric acid by the action of phosphoric oxide :—

$$
\begin{array}{lllllllll}
SO_3.H_2O & + & MgO & = & SO_3.MgO & + & H_2O \\
SO_3.H_2O & + & P_2O_5 & = & P_2O_5.H_2O & + & SO_3.
\end{array}
$$

3. $SO_2.O_2H_2$, or $SO_2(OH)_2$. This formula represents such reactions as the elimination of hydrogen dioxide by the action of barium dioxide, BaO_2.

4. $SH_2.O_4$. This formula represents the formation of sulphuric acid by direct oxidation of hydrogen sulphide, SH_2, and the elimination of the latter by the action of ferrous sulphide :—

$$SH_2.O_4 + FeS = FeSO_4 + SH_2.$$

Formulæ of the third of these types, like $SO_2(OH)_2$, which represent oxygen-acids as compounds of hydroxyl with certain acid radicles, as SO_2'' (sulphuryl), CO'' (carbonyl), PO''' (phosphoryl), &c., correspond with a great variety of reactions, and are of very frequent use. They exhibit in particular the relation of the oxygen-acids (hydroxylates) to the corresponding chlorides, *e.g.* :—

$(SO_2)(OH)_2$ **Sulphuric acid.**	$(SO_2)Cl_2$ **Sulphuric chloride.**
$(PO)(OH)_3$ **Phosphoric acid.**	$(PO)Cl_3$ **Phosphoric chloride.**

Basicity of Acids.—Normal, Acid and Double Salts.—Acids are monobasic, bibasic, tribasic, &c., according as they contain one or more atoms of hydrogen replaceable by metals; thus nitric acid, HNO_3, and hydrochloric acid, HCl, are monobasic; sulphuric acid, H_2SO_4, is bibasic; phosphoric acid, H_3PO_4, is tribasic.

Monobasic acids form but one class of salts by substitution, the metal taking the place of the hydrogen in one, two, or three molecules of the acid, according to its equivalent value or atomicity; thus the action of hydrochloric acid on sodium, zinc, and aluminium is represented by the equations :

$$
\begin{array}{lllllll}
HCl & + & Na & = & NaCl & + & H \\
2HCl & + & Zn & = & ZnCl_2 & + & H_2 \\
3HCl & + & Al & = & AlCl_3 & + & H_3,
\end{array}
$$

and that of nitric acid on the hydroxides of the same metals by the equations :

$$
\begin{array}{lllllll}
HNO_3 & + & Na(HO) & = & NaNO_3 & + & H(HO) \\
2HNO_3 & + & Ba(HO)_2 & = & Ba(NO_3)_2 & + & 2H(HO) \\
3HNO_3 & + & Al(HO)_3 & = & Al(NO_2)_3 & + & 3H(HO).
\end{array}
$$

Bibasic acids, on the other hand, form two classes of salts, viz, *primary* or *acid salts*, in which half the hydrogen is replaced by a metal; and *secondary salts*, in which the whole of the hydrogen is thus replaced, the salt being called *normal* or *neutral*, if it contains one metal, and *double* if it contains two metals; thus:

From H_2SO_4	is derived	$KHSO_4$	hydro-potassic sulphate, primary, or acid potassium sulphate,
„ „	„	K_2SO_4	bipotassic sulphate, secondary, or normal sulphate,
„ „	„	$BaSO_4$	barium sulphate,
„ $2H_2SO_4$	„	$NaK_3(SO_4)_2$	sodio-tripotassic sulphate,
„ „	„	$KAl(SO_4)_2$	potassio-aluminic sulphate,
„ $3H_2SO_4$	„	$Al_2(SO_4)_3$	normal aluminium sulphate.

Tribasic acids in like manner form two classes of acid salts, *primary* or *secondary*, according as one-third or two-thirds of the hydrogen is replaced by a *metal*; also *tertiary salts*, including *normal* and *double* or *triple salts*, in which the hydrogen is wholly replaced by one or more metals; in quadribasic acids the variety is of course still greater.

The use of the terminations *ous* and *ic*, as applied to salts, has already been explained. We have only further to observe in this place that when a metal forms but one class of salts, it is for the most part better to designate those salts by the name of the metal itself than by an adjective ending in *ic*; thus *potassium nitrate*, and *lead sulphate*, are mostly to be preferred to *potassic nitrate* and *plumbic sulphate*. But in naming double salts, and in many cases where a numeral prefix is required, the names ending in *ic* are more euphonious; thus *triplumbic phosphate* sounds better than *trilead phosphate*, and *hydrodisodic phosphate* is certainly better than *hydrogen* and *disodium phosphate*; but there is no occasion for a rigid adherence to either system.

All oxygen-salts may also be represented as compounds of an acid oxide with one or more molecules of the same or different basic oxides, including water, *e.g.*:

Hydro-potassic sulphate, $2HK(SO_4) = H_2O.K_2O.2SO_3$
Sodio-tripotassic sulphate, $2NaK_3(SO_4)_2 = Na_2O.3K_2O.4SO_4$
Potassio-aluminic sulphate, $2KAl(SO_4)_2 = K_2O.Al_2O_3.4SO_3$
Hydrodisodic phosphate, $2HNa_2(PO_4) = H_2O.2Na_2O.P_2O_5$.

When a normal oxygen-salt is thus formulated, it is easy to see that the number of molecules of acid oxide contained in its molecule is equal to the number of oxygen-atoms in the base; thus:

Normal potassium sulphate, $K_2SO_4 = K_2O.SO_3$
„ barium sulphate, $BaSO_4 = BaO.SO_3$
„ stannic sulphate, $Sn(SO_4)_2 = SnO_2.2SO_3$
„ aluminium sulphate, $Al_2(SO_4)_3 = Al_2O_3.3SO_3$.

When the proportion of acid oxide is less than this, the salt is called basic; such salts may be regarded as compounds of a normal salt with one or more molecules of basic oxide, or as derived from normal salts by substitution of oxygen for an equivalent quantity of the acid radicle ; thus :

$$\begin{array}{lll} \text{Tribasic lead nitrate,} & 3PbO.N_2O_5 & = Pb(NO_3)_2.2PbO \\ & & = Pb_3(NO_3)_2O_2 \\ \left.\begin{array}{c}\text{Quadribasic alumi-}\\ \text{nium sulphate,}\end{array}\right\} & 4Al_2O_3.3SO_3 & = 3Al_2O_3.Al_2(SO_4)_3 \\ & & = Al_8(SO_4)_3O_9\,. \end{array}$$

The last mode of formulation exhibits the analogy of these basic oxysalts to the oxychlorides, oxyiodides, &c. ; thus the basic lead nitrate, $Pb_3(NO_3)_2O_2$, just mentioned, is analogous to the oxychloride of that metal, $Pb_3Cl_2O_2$, which occurs native as mendipite.

The terms basic and acid are sometimes applied to salts with reference to their action on vegetable colours. The normal salts formed by the union of the stronger acids with the alkalis and alkaline earths, such as potassium sulphate, K_2SO_4, barium nitrate, $Ba(NO_3)_2$, &c., are perfectly neutral to vegetable colours, but most other normal salts exhibit either an acid or an alkaline reaction ; thus ferrous sulphate, cupric sulphate, silver nitrate, and many others, redden litmus, while the normal carbonates and phosphates of the alkali-metals exhibit a decided alkaline reaction. It is clear, then, that the action of a salt on vegetable colours bears no definite relation to its composition : hence the term *normal*, as applied to salts in which the basic hydrogen of the acid is wholly replaced, is preferable to *neutral*, and the terms *basic* and *acid*, as applied to salts, are best used in the manner above explained with reference to their composition.

When a normal salt containing a monoxide passes by oxidation to a salt containing a sesquioxide, dioxide, or trioxide, the quantity of acid present is no longer sufficient to saturate the base. Thus when a solution of ferrous sulphate, $FeSO_4$, or $FeO.SO_3$ (common green vitriol), is exposed to the air, it absorbs oxygen, and an insoluble ferric salt is produced containing an excess of base, while normal ferric sulphate remains in solution :

$$\underset{\text{Ferrous sulphate.}}{4(FeO.SO_3)} + O_2 = \underset{\substack{\text{Normal ferric}\\ \text{sulphate.}}}{Fe_2O_3.3SO_3} + \underset{\substack{\text{Basic ferric}\\ \text{sulphate.}}}{Fe_2O_3.SO_3}\,.$$

These basic salts are very often insoluble in water.

Salts containing a proportion of acid oxide larger than is sufficient to form a neutral compound are called anhydro-salts (sometimes, though improperly, acid salts ; they may evidently be regarded as compounds of a normal salt with excess of acid oxide ; *e.g.* :

$$\begin{array}{lll} \left.\begin{array}{l}\text{Sodium anhydrosulphate*}\\ \quad\text{(bisulphate of soda),}\end{array}\right\} & Na_2O.(SO_3)_2 & = Na_2(SO_4)SO_3 \\ \left.\begin{array}{l}\text{Potassium anhydrochromate}\\ \quad\text{(bichromate of potash),}\end{array}\right\} & K_2O.(CrO_3)_2 & = K_2(CrO_4).CrO_3\,. \end{array}$$

---

* The so-called "anhydrosulphates" are now regarded as salts of a distinct acid, pyrosulphuric acid, $H_2S_2O_7$ (p. 212).

The following is a list of the most important inorganic acids arranged according to their basicity :—

Monobasic Acids.

Hydrochloric,	HCl	Boric,	HBO_2
Hydrobromic,	HBr	Antimonic,	$HSbO_3$
Hydriodic,	HI	Hypochlorous,	$HClO$
Hydrofluoric,	HF	Chlorous,	$HClO_2$
Nitrous,	HNO_2	Chloric,	$HClO_3$
Nitric,	HNO_3	Perchloric,	$HClO_4$
Hyposulphurous,	$H.SHO_2$	Bromic,	$HBrO_3$
Hypophosphorous,	$H(PH_2O_2)$	Iodic,	HIO_3
Metaphosphoric,	HPO_3	Periodic,	HIO_4

Bibasic Acids.

Hydric (water),	H_2OH	Selenious,	H_2SeO_3
Sulphydric,	H_2S	Selenic,	H_2SeO_4
Selenhydric,	H_2Se	Tellurous,	H_2TeO_3
Tellurhydric,	H_2Te	Telluric,	H_2TeO_4
Sulphurous,	H_2SO_3	Manganic,	H_2MnO_4
Sulphuric,	H_2SO_4	Permanganic,	$H_2Mn_2O_8$
Pyrosulphuric,	$H_2S_2O_7$	Chromic,	H_2CrO_4
Thiosulphuric,	$H_2S_2O_3$	Stannic,	H_2SnO_3
Dithionic,	$H_2S_2O_6$	Metasilicic,	H_2SiO_3
Trithionic,	$H_2S_3O_6$	Carbonic,	H_2CO_3
Tetrathionic,	$H_2S_4O_6$	Phosphorous,	$H_2(PHO_3$
Pentathionic,	$H_2S_5O_6$		

Tribasic Acids.

Orthophosphoric,	H_3PO_4	Arsenic,	H_3AsO_4

Tetrabasic Acids.

Pyrophosphoric,	$H_4P_2O_7$	Orthosilicic,	H_4SiO_4

The general characters of most of the non-metallic acids and their salts have been already considered; but the phosphates require further notice.

PHOSPHATES.—There are three modifications of phosphoric acid: one being monobasic, the second tribasic, and the third tetrabasic, as indicated in the preceding table.

Hydrogen phosphide, PH_3, burnt in air or oxygen gas, takes up four atoms of oxygen, and forms trihydric phosphate or tribasic phosphoric acid, PH_3O_4. The same acid is produced by the oxidation of hypophosphorous or phosphorous acid; by oxidising phosphorus with nitric acid (p. 237); by the decomposition of native calcium phosphate (apatite) and other native phosphates; and by the action of boiling water on phosphorus pentoxide, P_2O_5.

$$2NaPO_3 + Pb(NO_3)_2 = Pb(PO_3)_2 +$$

and this lead-salt decomposed by sulphydric ac
hydric acid having the composition HPO_3, p
quite distinct from those of the trihydric acid al

$$Pb(PO_3)_2 + H_2S = 2HPO_3 +$$

The trihydric acid which is produced by the oxid
and by the decomposition of the ordinary native
orthophosphoric acid or ordinary phos
monohydric acid is called metaphosphoric
may be regarded as a trihydrate, the latter a
phosphoric oxide:—

$$2H_3PO_4 = P_2O_5.3H_2O\text{, orthophosph}$$
$$2HPO_3 = P_2O_5.H_2O\text{, metaphosphor}$$

Both are soluble in water, and the former may
action of boiling water, the latter by that of cold
oxide. They are easily distinguished from on
reactions with albumin and with silver nitrat
acid coagulates albumin, and gives a white pre
nitrate; whereas orthophosphoric acid does not
and gives no precipitate, or a very slight one,
till it is neutralised with an alkali, in which case
is formed.

Metaphosphoric acid and its salts differ from o
and the orthophosphates by the want of one or
or base; thus:—

Metaphosphates.		Orthophosphates.		
HPO_3	=	H_3PO_4	–	]
$NaPO_3$	=	NaH_2PO_4	–	]

metallic orthophosphates (see the first three equations above).—*β.* The metaphosphate of a heavy metal, silver or lead, for example, is converted by boiling with water into a trimetallic phosphate and orthophosphoric acid:—

$$3AgPO_3 + 3H_2O = Ag_3PO_4 + 2H_3PO_4.$$

γ. When any metaphosphate is fused with an oxide, hydrate, or carbonate, it becomes a trimetallic orthophosphate, *e.g.:*

$$NaPO_3 + Na_2CO_3 = Na_3PO_4 + CO_2.$$

On the other hand (*δ*), when orthophosphoric acid is heated to redness, it loses water and becomes metaphosphoric acid; and when a monometallic orthophosphate is heated to redness, it also loses water and is transformed into a metaphosphate.

Intermediate between orthophosphates and metaphosphates, there are at least three distinct classes of salts, the most important of which are the pyrophosphates or paraphosphates, which may be derived from the tetrahydric or quadribasic acid, $H_4P_2O_7$, the normal sodium salt, for example, being $Na_4P_2O_7$, the normal lead salt, $Pb_2P_2O_7$, &c. These salts may be viewed as compounds of orthophosphate and metaphosphate, *e.g.:*

$$Na_4P_2O_7 = Na_3PO_4 + NaPO_3.$$

Sodium pyrophosphate is produced by heating disodic orthophosphate to redness, a molecule of water being then given off:

$$2Na_2HPO_4 = H_2O + Na_4P_2O_7.$$

The aqueous solution of this salt yields insoluble pyrophosphates with lead and silver salts; thus with lead nitrate:

$$Na_4P_2O_7 + 2Pb(NO_3)_2 = 4NaNO_3 + Pb_2P_2O_7;$$

and lead pyrophosphate decomposed by hydrogen sulphide yields hydrogen pyrophosphate or pyrophosphoric acid:

$$Pb_2P_2O_7 + 2H_2S = 2PbS + H_4P_2O_7.$$

Pyrophosphoric acid is distinguished from metaphosphoric acid by not coagulating albumin and not precipitating neutral solutions of barium or silver salts, and from orthophosphoric acid by producing a white instead of a yellow precipitate with silver nitrate.

Pyrophosphates are easily converted into metaphosphates and orthophosphates, and *vice versâ*, by addition or abstraction of water or a metallic base.

α. The production of a pyrophosphate from an orthophosphate by loss of water has been already mentioned.—*β.* Conversely when a pyrophosphate is heated with water or a base, it becomes an orthophosphate, *e.g.:*

$$\begin{aligned} Na_4P_2O_7 + H_2O &= 2Na_2HPO_4 \\ Na_4P_2O_7 + 2NaHO &= 2Na_3PO_4 + H_2O. \end{aligned}$$

In like manner orthophosphoric acid heated to 215° is almost entirely converted into pyrophosphoric acid: $2H_3PO_4 - H_2O = H_4P_2O_7$; and conversely, when pyrophosphoric acid is boiled with water, it is transformed into orthophosphoric acid.

γ. Pyrophosphoric acid heated to dull redness is converted into metaphosphoric acid: $H_4P_2O_7 - H_2O = 2HPO_3$. The converse reaction is not easily effected, inasmuch as metaphosphoric acid by absorbing water generally passes directly to the state of orthophosphoric acid. Peligot, however, observed the formation of pyrophosphoric from metaphosphoric acid by very slow absorption of water. —*δ*. When a metallic metaphosphate is treated with a proper proportion of a hydroxide, oxide, or carbonate, it is converted into a pyrophosphate; thus:

$$\begin{array}{ccccccc} 2NaPO_3 & + & Na_2CO_3 & = & Na_4P_2O_7 & + & CO_2. \\ \text{Metaphosphate.} & & \text{Carbonate.} & & \text{Pyrophosphate.} & & \text{Carbon dioxide.} \end{array}$$

Fleitmann and Henneberg, by fusing together a molecule of sodium pyrophosphate, $Na_3PO_4.NaPO_3$, with two molecules of metaphosphate, $NaPO_3$, obtained a salt having the composition, $Na_3PO_4.3NaPO_3 = Na_6P_4O_{13}$, which is soluble without decomposition in a small quantity of hot water, and crystallises from its solution by evaporation over oil of vitriol. An excess of hot water decomposes it, but its cold aqueous solution is moderately permanent. Insoluble phosphates of similar composition may be obtained from the sodium-salt by double decomposition. Fleitmann and Henneberg obtained another crystallisable but very insoluble salt, having the composition, $Na_3PO_4.9NaPO_3 = Na_{12}P_{10}O_{31}$, by fusing together one molecule of sodium pryophosphate with eight molecules of the metaphosphate; and insoluble phosphates of similar constitution were obtained from it by double decomposition.

The comparative composition of these different phosphates is best shown by representing them as compounds of phosphoric oxide with metallic oxide, and assigning to them all the quantity of base contained in the most complex member of the series; thus—

Orthophosphate, ...	$6Na_2O.2P_2O_5 = 4Na_3PO_4$
Pyrophosphate, ...	$6Na_2O.3P_2O_5 = 3Na_4P_2O_7$
Fleitmann and Henneberg's phosphate (*a*),	$6Na_2O.4P_2O_5 = 2Na_6P_4O_{13}$
" " " (*b*),	$6Na_2O.5P_2O_5 = Na_{12}P_{10}O_{31}$
Metaphosphate, ...	$6Na_2O.6P_2O_5 = 12NaPO_3$.

Metallic Sulphides.—These compounds correspond, for the most part, in composition with the oxides: thus there are two sulphides of arsenic, As_2S_3 and As_2S_5, corresponding with the oxides, As_2O_3 and As_2O_5; also two sulphides of mercury, Hg_2S and HgS, analogous to the oxides, Hg_2O and HgO. Occasionally, however, we meet with oxides to which there are no corresponding sulphides (manganese dioxide, for example), and more frequently sulphides to which there are no corresponding oxides, the most remarkable of which are perhaps the alkaline polysulphides. Potassium, for example, forms the series of sulphides, K_2S, K_2S_2, K_2S_3, K_2S_4, and K_2S_5, the third and fifth of which have no analogues in the oxygen series.

There are also hydrosulphides analogous to the hydroxides, and containing the elements of a metallic sulphide and hydrogen sulphide, or sulphydric acid: *e.g.*, potassium hydrosulphide, $K_2S.H_2S = 2KHS$; lead hydrosulphide, $PbS.H_2S = PbH_2S_2$. Hydrosulphides and sulphides may be derived from sulphydric acid by partial or total replacement of the hydrogen by metals, just as metallic hydroxides and oxides are derived from water.

Many metallic sulphides occur as natural minerals, especially the sulphides of lead, copper, and mercury, which afford valuable ores for the extraction of the metals, and iron bisulphide or iron pyrites, FeS_2, which is largely used as a source of sulphur, and for the preparation of ferrous sulphate.

Sulphides are formed artificially by heating metals with sulphur; by the action of metals on gaseous hydrogen sulphide; by the reduction of sulphates with hydrogen or charcoal; by heating metallic oxides in contact with gaseous hydrogen sulphide or vapour of carbon bisulphide; and by precipitation of metallic solutions with hydrogen sulphide or a sulphide of alkali-metal. Some metals, as copper, lead, silver, bismuth, mercury, and cadmium, are precipitated from their acid solutions by hydrogen sulphide, passed into them as gas, or added in aqueous solution, the sulphides of these metals being insoluble in dilute acids; others, as iron, cobalt, nickel, manganese, zinc, and uranium, form sulphides which are soluble in acids, and these are precipitated by hydrogen sulphide only from alkaline solutions, or by ammonium or potassium sulphide from neutral solutions. Many of these sulphides exhibit characteristic colours, which serve as indications of the presence of the respective metals in solution (p. 217).

Metallic sulphides are also formed by the reduction of sulphates with organic substances; many native sulphides have doubtless been formed in this way.

The physical characters of some metallic sulphides closely resemble those of the metals in certain particulars, such as the peculiar opacity, lustre, and density, especially when they are in a crystalline condition. They are generally crystallisable, brittle, and of a grey, pale yellow, or dark brown colour. The sulphides of the alkali-metals are soluble in water; most of the others are insoluble. They are more frequently fusible than the corresponding oxides, and some are volatilisable; as mercury sulphide and arsenic sulphide.

Many sulphides, when heated out of contact with atmospheric air, do not undergo any decomposition; this is the case chiefly with those containing the smallest proportions of sulphur, such as the monosulphides of iron and zinc. Sulphides containing larger proportions of sulphur are partially decomposed by heat, losing part of their sulphur, and being converted into lower sulphides; as in the case of iron bisulphide. The sulphides of gold and platinum are completely reduced by heat.

sulphates by this means. Zinc, iron, mangan
bismuth sulphides are converted into oxides, a
is produced: but when the temperature is not
some sulphate is formed by direct oxidation.
sulphides are completely reduced to the metallic
sulphides gradually undergo alteration by mere
but it is then generally limited to the prod
unless the oxidation takes place so rapidly tha
is sufficient to decompose the sulphate first
production of some metals for use in the art
sulphur from the native minerals is effected
this action in the operation of roasting.

Metallic sulphides are decomposed in like m
with metallic oxides in suitable proportions,
oxide and the metal of both the sulphide a
reduced from the native sulphide in this manne

Many metallic sulphides are decomposed b
of water, sulphuretted hydrogen being evolve
enters into combination with the chlorous
Nitric acid when concentrated decomposes m
formation of metallic oxide, sulphuric acid, su
oxide of nitrogen. Nitromuriatic acid acts in a
still more energetically.

Sulphur-Salts.—The sulphides of the more b
with those of the more chlorous or electro-neg
the non-metallic elements, forming sulphur-
composition to the oxygen-salts, *e.g.*:

Carbonate, K_2CO_3 = K_2
Sulphocarbonate, K_2CS_3 = K_2

CLASS I.—MONAD METALS.

GROUP. I.—METALS OF THE ALKALIS.

POTASSIUM.

Atomic weight, 39·1. Symbol, K (Kalium).

Potassium was discovered in 1807 by Sir H. Davy, who obtained it in very small quantity by exposing a piece of moistened potassium hydroxide to the action of a powerful voltaic battery, the alkali being placed between a pair of platinum plates connected with the apparatus. Processes have since been devised for obtaining this metal in almost any quantity that can be desired.

An intimate mixture of potassium carbonate and charcoal is prepared by calcining, in a covered iron pot, the crude tartar of commerce; when cold it is rubbed to powder, mixed with one tenth part of charcoal in small lumps, and quickly transferred to a retort of stout hammered iron: the latter may be one of the iron bottles in which mercury is imported. The retort is introduced into a furnace *a* (fig. 142), and placed horizontally on supports of fire brick, *f*, *f*. A wrought iron tube *d*, four inches long, serves to convey the vapours of potassium into a receiver *e*, formed of two pieces of wrought iron, *a*, *b* (fig. 143), which are fitted closely to each other so as to form a shallow box only a quarter of an inch deep, and are kept together by clamp-screws. The iron plate should be one-sixth of an inch thick, twelve inches long, and five inches wide. The receiver is open at both ends, the socket fitting upon the neck of the iron bottle. The object of giving the receiver this flattened form is to ensure the rapid cooling of the potassium, and thus to withdraw it from the action of the carbon monoxide, which is disengaged during the entire process, and has a strong tendency to unite with the potassium, forming a dangerously explosive compound. Before connecting the receiver with the tube *d*, the fire is slowly raised till the iron bottle attains a dull red heat. Powdered vitrefied borax is then sprinkled upon it, which melts and forms a coating, serving to protect the iron from oxidation. The heat is then to be urged until it is very intense, care being taken to raise it as equally as possible throughout every part of the furnace. When a full reddish-white heat is attained, vapours of potassium begin to appear and burn with a bright flame. The receiver is then adjusted to the end of the tube, which must not project more than a quarter of an inch through the iron plate forming the front wall of the furnace; otherwise the tube is liable to be obstructed by the accumulation of solid potassium, or of the explosive compound above mentioned. Should any obstruction occur, it must be removed by thrusting in an iron bar, and, if this fail, the fire must be immediately withdrawn by removing the bars from the furnace, with the exception of two which support the iron bottle. The receiver is kept cool by the application of a wet cloth to its outside. When the operation is complete, the receiver with the potassium is removed and immediately plunged into a vessel of rectified petroleum provided with a cover, and kept cool by immersion in water. When the apparatus is sufficiently cooled, the potassium is detached and preserved under petroleum.

Fig. 142.

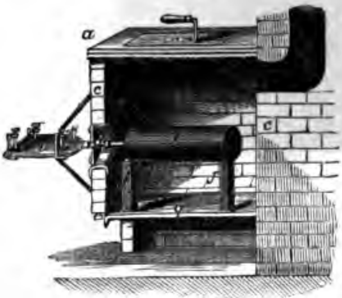
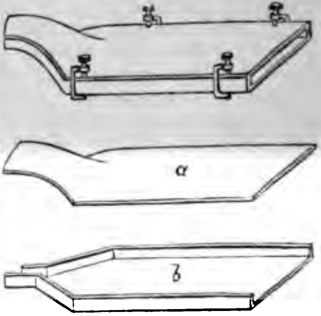


Fig. 143.



If the potassium be wanted absolutely pure, it must be afterwards re-distilled in an iron retort, into which some naphtha has been put, that its vapour may expel the air, and prevent oxidation of the metal.

Potassium is a brilliant white metal, with a high degree of lustre; at the common temperature of the air it is soft, and may be easily cut with a knife, but at 0° it is brittle and crystalline. It melts completely at 62·5°, and distils at a low red heat. It floats on water, its specific gravity being only 0·865.

Exposed to the air, potassium oxidises instantly, a tarnish covering the surface of the metal, which quickly thickens to a crust of caustic potash. Thrown upon water, it takes fire spontaneously, and burns with a beautiful purple flame, yielding an alkaline solution. When it is brought into contact with a little water in a jar standing over mercury, the liquid is decomposed with great energy, and hydrogen liberated. Potassium is always preserved under the surface of petroleum.

Potassium Chloride, KCl.—This salt is obtained in large quantity in the manufacture of the chlorate; it is easily purified from any portions of the latter by exposure to a dull red-heat. Within the last few years large quantities of this salt have been obtained from sea-water, by a peculiar process suggested by M. Balard.* It is also contained in kelp, and is separated for the use of the alum-maker. Considerable quantities of it are now obtained from the salt-beds of Stassfurt, near Magdeburg, in Prussia.

Potassium chloride closely resembles common salt in appearance, assuming, like that substance, the cubic form of crystallisation. The crystals dissolve in three parts of cold, and in a much smaller quantity of boiling water: they are anhydrous, have a simple saline taste, with slight bitterness, and fuse when exposed to a red heat. Potassium chloride is volatilised by a very high temperature.

Potassium Iodide, KI.—There are three different methods of preparing this important medicinal compound.

(1.) When iodine is added to a strong solution of caustic potash free from carbonate, it is dissolved in large quantity, forming a colourless solution containing potassium iodide and iodate; the reaction is the same as in the analogous case with chlorine. When the solution begins to be permanently coloured by the iodine, it is evaporated to dryness, and cautiously heated to redness, by which the iodate is entirely converted into iodide. The mass is then dissolved in water, and, after filtration, made to crystallise.

(2.) Iodine, water, and iron-filings or scraps of zinc, are placed in a warm situation until the combination is complete, and the solution colourless. The resulting iodide of iron or zinc is then filtered, and exactly decomposed with solution of pure potassium carbonate, great care being taken to avoid excess of the latter. Potassium iodide and ferrous carbonate, or zinc carbonate, are thus obtained: the former is separated by filtration, and evaporated until the solution is sufficiently concentrated to crystallise on cooling, the washings of the filter being added to avoid loss:

$$FeI_2 + K_2CO_3 = 2KI + FeCO_3.$$

(3.) A very simple method for the preparation of potassium iodide was proposed by Liebig. One part of amorphous phosphorus is added to 40 parts of warm water; 20 parts of dry iodine are then gradually added and intimately mixed with the phophorus by trituration. The dark-brown liquid thus obtained is now heated on the water-bath until it becomes colourless; it is then poured off from the undissolved phosphorus, and neutralised, first with barium carbonate and then with baryta-water, until it becomes slightly alkaline; and the insoluble barium phosphate is filtered off and washed. The filtrate now contains nothing but barium iodide, which, when treated with potassium sulphate, yields insoluble barium sulphate and potassium iodide in solution. Lime answers nearly as well as baryta.

Potassium iodide crystallises in cubes, which are often, from some unexplained cause, milk-white and opaque: they are anhydrous, and fuse readily when heated. The salt is very soluble in water, tinguishable in appearance and general chara

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* Reports by the Juries of the International Exhibition of 1862, Class II.

Potassium Oxides.—Potassium combines proportions, forming a monoxide, K_2O, a diox K_2O_4, and three oxides intermediate between a hydroxide, KHO, corresponding with the m

Potassium monoxide, K_2O, also called *anhyd* is formed when potassium in thin slices is expos atures to dry air free from carbon dioxide; als is heated with an equivalent quantity of meta

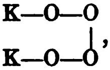
$$2KHO + K_2 = 2K_2O +$$

It is white, very deliquescent and caustic, c with water, forming potassium hydroxide, and when moistened with it; melts at a red heat, high temperatures.

The *dioxide*, K_2O_2, or

$$\begin{array}{c}KO\\ |\\ KO\end{array}$$

, is formed at a preparation of the tetroxide, but has not bee By carefully regulating the heat and supply o of the potassium may be converted into a whit the composition of the dioxide. An aqueous is formed by the action of water on the tetroxi

The *tetroxide*, K_2O_4, or 

$$\begin{array}{l}K\text{—}O\text{—}O\\ \quad\quad\quad\;\; |\\ K\text{—}O\text{—}O\end{array}$$

, is prod is burnt in excess of dry air or oxygen gas. powder, which cakes together at about 280°. rapidly, and is decomposed by water, giving of

POTASSIUM HYDROXIDE, KHO, commonly called *caustic potash*, or *potassa*, is a very important substance, and one of great practical utility. It is always prepared by decomposing the carbonate with calcium hydroxide (slaked lime). 10 parts of potassium carbonate are dissolved in 100 parts of water, and heated to ebullition in a clean untinned iron, or, still better, silver vessel; 8 parts of good quicklime are meanwhile slaked in a covered basin, and the resulting calcium hydroxide is added, little by little, to the boiling solution of carbonate, with frequent stirring. When all the lime has been introduced, the mixture is suffered to boil for a few minutes, and then removed from the fire and covered up. In the course of a very short time, the solution will have become quite clear, and fit for decantation, the calcium carbonate, with the excess of hydrate, settling down as a heavy, sandy precipitate. The solution should not effervesce with acids.

It is essential in this process that the solution of potassium carbonate be dilute, otherwise the decomposition becomes imperfect. The proportion of lime recommended is much greater than that required by theory, but it is always proper to have an excess.

The solution of potassium hydroxide may be concentrated by quick evaporation in the iron or silver vessel to any desired extent; when heated until vapour of water ceases to be disengaged, and then suffered to cool, it furnishes the solid hydroxide, KHO or $K_2O.H_2O$.

Pure potassium hydroxide is also easily obtained by heating to redness for half an hour in a covered copper vessel, one part of pure powdered nitre with two or three parts of finely divided copper foil. The mass, when cold, is treated with water.

Potassium hydroxide is a white solid substance, very deliquescent, and soluble in water; alcohol also dissolves it freely, which is the case with comparatively few potassium compounds: the solid hydroxide of commerce, which is very impure, may thus be purified. The solution of this substance possesses, in the very highest degree, the properties termed alkaline: it restores the blue colour to litmus which has been reddened by an acid; neutralises completely the most powerful acids; has a nauseous and peculiar taste; and dissolves the skin, and many other organic matters, when the latter are subjected to its action. It is frequently used by surgeons as a cautery, being moulded into little sticks for that purpose.

Potassium hydroxide, both in the solid state and in solution, rapidly absorbs carbonic acid from the air: hence it must be kept in closely stopped bottles. When imperfectly prepared, or partially altered by exposure, it effervesces with an acid. It is not decomposed by heat, but volatilises undecomposed at a very high temperature.

The following table of the densities and value in anhydrous potassium oxide, K_2O, of different solutions of potassium hydroxide is given on the authority of Dalton:—

Density.	Percentage of K_2O.
1·68	51·2
1·60	46·7
1·52	42·9
1·47	39·6
1·44	36·8
1·42	34·4
1·39	32·4
1·36	29·4
1·33	26·3
1·28	23·4
1·23	19·5
1·19	16·2
1·15	13·0
1·11	9·5
1·06	4·7

Potassium Nitrate; *Nitre; Saltpetre*, $KNO_3 = NO_2(OK)$.—This important compound is a natural product, being disengaged by a kind of efflorescence from the surface of the soil in certain dry and hot countries. It may also be produced by artificial means, namely, by the oxidation of ammonia in presence of a powerful base.

In France, large quantities of artificial nitre are prepared by mixing animal refuse of all kinds with old mortar or slaked lime and earth, and placing the mixture in heaps, protected from the rain by a roof, but freely exposed to the air. From time to time the heaps are watered with putrid urine, and the mass is turned over, to expose fresh surfaces to the air. When much salt has been formed, the mixture is lixiviated, and the solution, which contains calcium nitrate, is mixed with potassium carbonate; calcium carbonate is formed, and the nitric acid transferred to the alkali. The filtered solution is then made to crystallise, and the crystals are purified by re-solution and crystallisation, the liquid being stirred to prevent the formation of large crystals.

The greater part of the nitre used in this country comes from India: it is dissolved in water, a little potassium carbonate is added to precipitate lime, and then the salt is purified as above.

Considerable quantities of nitre are now manufactured by decomposing native sodium nitrate (Chile saltpetre), with carbonate or chloride of potassium. In Belgium the potassium carbonate obtained from the ashes of the beetroot sugar manufactories is largely used for this purpose; the potassium nitrate thus prepared is very pure, and is produced at a low price.

Potassium nitrate crystallises in anhydrous six-sided prisms, with dihedral summits, belonging to the rhombic or trimetric system: it is soluble in 7 parts of water at 15·5°, and in its own weight of boiling water. Its taste is saline and cooling, and it is without action on vegetable colours. It melts at a temperature below redness, and is completely decomposed by a strong heat.

When it is thrown on the surface of many metals in a state of fusion, or mixed with combustible matter and heated, rapid oxidation ensues, at the expense of the oxygen of the nitric acid. Examples of such mixtures are found in common gunpowder, and in nearly all pyrotechnic compositions, which burn in this manner independently of the oxygen of the air, and even under water. Gunpowder is made by very intimately mixing together potassium nitrate, charcoal, and sulphur, in proportions which approach 2 molecules of nitre, 3 atoms of carbon, and 1 atom of sulphur.

These quantities give, reckoned to 100 parts, and compared with the proportions used in the manufacture of the English Government powder, the following results :—

	Theory.	Proportions in practice.
Potassium nitrate, . .	74·8	75
Charcoal, ...	13·3	15
Sulphur, ...	11·9	10
	100·0	100

The nitre is rendered very pure by the means already mentioned, freed from water by fusion, and ground to fine powder ; the sulphur and charcoal, the latter being made from light wood, as dogwood or alder, are also finely ground, after which the materials are weighed out, moistened with water, and thoroughly mixed by grinding under an edge-mill. The mass is then subjected to great pressure, and the mill-cake thus produced broken in pieces, and placed in sieves made of perforated vellum, moved by machinery, each containing, in addition, a round piece of heavy wood. The grains of powder broken off by attrition fall through the holes in the skin, and are easily separated from the dust by sifting. The powder is, lastly, dried by exposure to steam-heat, and sometimes glazed or polished by agitation in a kind of cask mounted on an axis.

It was formerly supposed that when gunpowder is fired, the whole of the oxygen of the potassium nitrate was transferred to the carbon, forming carbon dioxide, the sulphur combining with the potassium, and the nitrogen being set free. There is no doubt that this reaction does take place to a considerable extent, and that the large volume of gas thus produced, and still further expanded by the very high temperature, sufficiently accounts for the explosive effects. But recent investigations by Bunsen, Karolyi, and others, have shown that the actual products of the combustion of gunpowder are much more complicated than this theory would indicate, a very large number of products being formed, and a considerable portion of the oxygen being transferred to the potassium sulphide, converting it into sulphate, which, in fact, constitutes the chief portion of the solid residue and of the smoke formed by the explosion.*

Potassium Chlorate, $KClO_3 = ClO_2(OK)$.—The theory of the production of chloric acid by the action of chlorine gas on a solution of caustic potash, has been already explained (p. 195). Chlorine gas is conducted by a wide tube into a strong and warm solution of potassium carbonate, until absorption of the gas ceases ; and the liquid is, if necessary, evaporated, and then left to cool, in order that the slightly soluble chlorate may crystallise out. The mother-liquor affords a second crop of crystals, but they are much more contaminated with potassium chloride. It may be purified by one or two re-crystallisations.

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* See Watts's Dictionary of Chemistry, vol. ii. p. 958.

Potassium chlorate is soluble in about 20 parts of cold and 2 of boiling water: the crystals are anhydrous, flat, and tabular; in taste it somewhat resembles nitre. When heated it gives off the whole of its oxygen as gas and leaves potassium chloride. By arresting the decomposition when the evolution of gas begins to slacken, and redissolving the salt, potassium perchlorate and chloride may be obtained.

This salt deflagrates violently with combustible matter, explosion often occurring by friction or blows. When about one grain-weight of chlorate and an equal quantity of sulphur are rubbed in a mortar, the mixture explodes with a loud report: hence it cannot be used in the preparation of gunpowder instead of the nitrate. Potassium chlorate is now a large article of commerce, being employed, together with phosphorus, in making instantaneous-light matches.

Potassium Perchlorate, $KClO_4 = ClO_3(OK.)$—This salt has been already noticed under the head of perchloric acid. It is best prepared by projecting powdered potassium chlorate into warm nitric acid, when the chloric acid is resolved into perchloric acid, chlorine and oxygen. The salt is separated from the nitrate by crystallisation. Potassium perchlorate is a very slightly soluble salt: it requires 55 parts of cold water, but is more freely taken up at a boiling heat.

potassic rocks with a mixture of calcium carbonate and fluoride. There are, however, natural processes at work, by which the potash is constantly being eliminated from these rocks. Under the influence of atmospheric agencies, these rocks disintegrate into soils, and as the alkali acquires solubility, it is gradually taken up by plants, and accumulates in their substance in a condition highly favourable to its subsequent applications.

Potassium-salts are always most abundant in the green and tender parts of plants, as may be expected, since from these, evaporation of nearly pure water takes place to a large extent: the solid timber of forest trees contains comparatively little.

In preparing the salt on an extensive scale, the ashes are subjected to a process called lixiviation : they are put into a large cask or tun, having, near the bottom, an aperture stopped by a plug, and a quantity of water is added. After some hours the liquid is drawn off, and more water added, that the whole of the soluble matter may be removed. The weakest solutions are poured upon fresh quantities of ash, in place of water. The solutions are then evaporated to dryness, and the residue is calcined, to remove a little brown organic matter : the product is the crude potash or pearlash of commerce, of which very large quantities are obtained from Russia and America. The salt is very impure : it contains potassium silicate, sulphate, chloride, &c.

The purified potassium carbonate of pharmacy is prepared from the crude article by adding an equal weight of cold water, agitating and filtering ; most of the foreign salts are, from their inferior degree of solubility, left behind. The solution is then boiled down to a very small bulk, and left to cool, when the carbonate separates in small crystals containing 2 molecules of water, $K_2CO_3.2H_2O$; these are drained from the mother-liquor, and then dried in a stove.

A still purer salt may be obtained by exposing to a red heat purified cream of tartar (acid potassium tartrate), and separating the carbonate by solution in water and crystallisation, or evaporation to dryness.

Potassium carbonate is extremely deliquescent, and soluble in less than its own weight of water: the solution is highly alkaline to test-paper. It is insoluble in alcohol. By heat the water of crystallisation is driven off, and by a temperature of full ignition the salt is fused, but not otherwise changed. This substance is largely used in the arts, and is a compound of great importance.

Acid potassium carbonate, Hydrogen and potassium carbonate, or *Monopotassic carbonate,* $KHCO_3$; commonly called *bicarbonate of potash.*—When a stream of carbonic acid gas is passed through a cold solution of potassium carbonate, the gas is rapidly absorbed, and a white, crystalline, less soluble substance separated, which is the acid salt. It is collected, pressed, redissolved in warm water, and the solution is left to crystallise.

Acid potassium carbonate is much less soluble than the normal carbonate, requiring 4 parts of cold water to dissolve it. The solution is nearly neutral to test-paper, and has a much milder taste than the normal salt. When boiled it gives off carbon dioxide. The crystals, which are large and beautiful, derive their form from a monoclinic prism: they are decomposed by heat, water and carbon dioxide being evolved, and normal carbonate left behind:

$$2KHCO_3 = K_2CO_3 + H_2O + CO_2.$$

Potassium Sulphates.—Potassium forms a normal or neutral sulphate, two acid sulphates, and an anhydrosulphate.

Normal potassium sulphate, or *Bipotassic sulphate*, $K_2SO_4 = SO_2(OK)_2 = K_2O.SO_3$, is obtained by neutralising the acid residue left in the retort when nitric acid is prepared, with crude potassium carbonate. The solution yields, on cooling, hard transparent crystals of the neutral sulphate, which may be re-dissolved in boiling water, and re-crystallised.

Potassium sulphate is soluble in about 10 parts of cold, and in a much smaller quantity of boiling water: it has a bitter taste, and is neutral to test-paper. The crystals are combinations of rhombic pyramids and prisms, much resembling those of quartz in figure and appearance: they are anhydrous, and decrepitate when suddenly heated, which is often the case with salts containing no water of crystallisation. They are quite insoluble in alcohol.

Acid potassium sulphate, Hydrogen and potassium sulphate, or *Monopotassic sulphate*, $KHSO_4 = SO_2(OK)(OH)$, commonly called *bisulphate of potash*.—To obtain this salt the neutral sulphate in powder is mixed with half its weight of oil of vitriol, and the whole evaporated quite to dryness in a platinum vessel placed under a chimney: the fused salt is dissolved in hot water and left to crystallise. The crystals have the figure of flattened rhombic prisms, and are much more soluble than the neutral salt, requiring only twice their weight of water at 15·5°, and less than half that quantity at 100°. The solution has a sour taste and strongly acid reaction.

Potassium Disulphate, or *Pyrosulphate*, $K_2S_2O_7$, derived from Nordhausen sulphuric acid, $H_2S_2O_7$, and commonly called *anhydrous bisulphate of potash*, is obtained by dissolving equal weights of the normal sulphate and oil of vitriol in a small quantity of warm distilled water, and leaving the solution to cool.

The pyro-sulphate crystallises out in long delicate needles, which if left for several days in the mother-liquor, disappear, and give place to crystals of the ordinary acid sulphate above described. This salt is decomposed by a large quantity of water, and is converted by strong fuming sulphuric acid into *hydropotassic pyrosulphate*, KHS_2O_7, which crystallises in transparent prisms. The neutral pyrosulphate in fine powder, heated with an alcoholic solution of potassium hydrosulphide, is converted with sulphate and thiosulphate, with evolution of hydrogen sulphide:

$$K_2S_2O_7 + 2KHS = K_2SO_4 + K_2S_2O_3 + H_2S.$$

Potassium Sulphides.—Potassium heated in sulphur vapour burns with great brilliancy. It unites with sulphur in five different proportions, forming the compounds K_2S, K_2S_2, K_2S_3, K_2S_4, K_2S_5; also a hydrosulphide or sulphydrate, KHS.

Monosulphide, K_2S.—It is doubtful whether this compound has been obtained in the pure state. It is commonly said to be produced by heating potassium sulphate in a current of dry hydrogen, or by igniting the same salt in a covered vessel with finely divided charcoal; but, according to Bauer, one of the higher sulphides is always formed at the same time, together with oxide of potassium. The product has a reddish-yellow colour, is deliquescent, and acts as a caustic on the skin. When potassium sulphate is heated in a covered crucible with excess of lamp-black, a mixture of potassium sulphide and finely divided carbon is obtained, which takes fire spontaneously on coming in contact with the air. The monosulphide might perhaps be obtained pure by heating 1 molecule of potassium sulphydrate, KHS, with 1 atom of the metal.

When sulphydric acid gas is passed to saturation into a solution of caustic potash, a solution of the sulphydrate is obtained, which is colourless at first, but if exposed to the air, quickly absorbs oxygen, and turns yellow, in consequence of the formation of bisulphide:

$$2KHS + O = K_2S_2 + H_2O.$$

If a solution of potash be divided into two parts, one half saturated with hydrogen sulphide, and then mixed with the other, a solution is formed which may contain potassium monosulphide:

$$KHS + KHO = K_2S + H_2O.$$

But it is also possible that the hydroxide and hydrosulphide may mix without mutual decomposition. The solution when mixed with one of the stronger acids, gives off hydrogen sulphide without deposition of sulphur, a reaction which is consistent with either view of its constitution.

The *bisulphide*, K_2S_2, is formed, as already observed, on exposing a solution of the hydrosulphide to the air till it begins to show turbidity. By evaporation in a vacuum, it is obtained as an orange-coloured, easily fusible substance.

The *trisulphide*, K_2S_3, is obtained by passing the vapour of carbon bisulphide over ignited potassium carbonate, as long as gas continues to escape:

$$2K_2CO_3 + 3CS_2 = 2K_2S_3 + 4CO + CO_2.$$

Also, together with potassium sulphate, forming one of the mixtures called *liver of sulphur*, by melting 552 parts (4 molecules) of potassium carbonate with 320 parts (10 atoms) of sulphur:

$$4K_2CO_3 + S_{10} = K_2SO_4 + 3K_2S_3 + 4CO_2.$$

The *tetrasulphide*, K_2S_4, is formed by reducing potassium sulphate with the vapour of carbon bisulphide.

The *pentasulphide*, K_2S_5, is formed by boiling a solution of any of the preceding sulphides with excess of sulphur till it is saturated, or by fusing either of them in the dry state with sulphur. The excess of sulphur then separates and floats above the dark brown pentasulphide.

Liver of sulphur, or *hepar sulphuris*, is a name given to a brownish substance, sometimes used in medicine, made by fusing together different proportions of potassium carbonate and sulphur. It is a variable mixture of the two higher sulphides with thiosulphate and sulphate of potassium.

When equal parts of sulphur and dry potassium carbonate are melted together at a temperature not exceeding 250°, the decomposition of the salt is quite complete, and all the carbon dioxide is expelled. The fused mass dissolves in water, with the exception of a little mechanically mixed sulphur, with dark-brown colour, and the solution is found to contain nothing besides pentasulphide and thiosulphate of potassium :

$$3K_2O + S_{12} = 2K_2S_5 + K_2S_2O_3.$$

When the mixture has been exposed to a temperature approaching that of ignition, it is found, on the contrary, to contain potassium sulphate, arising from the decomposition of the thiosulphate which then occurs :

$$4K_2S_2O_3 = K_2S_5 + 3K_2SO_4.$$

From both these mixtures the potassium pentasulphide may be extracted by alcohol, in which it dissolves.

When the carbonate is fused with half its weight of sulphur only, the trisulphide is produced, as above indicated, instead of the pentasulphide.

The effects described happen in the same manner when potassium hydroxide is substituted for the carbonate ; also, when a solution of the hydroxide is boiled with sulphur, a mixture of sulphide and thiosulphate always results.

Potassium-salts are colourless when not associated with a coloured metallic oxide or acid. They are all more or less soluble in water, and may be distinguished by the following characters :—

(1.) Solution of *tartaric acid*, added in excess to a moderately strong solution of a potassium-salt, gives, after some time, a white crystalline precipitate of cream of tartar ; the effect is greatly promoted by strong agitation.

(2.) Solution of *platinic chloride*, with a little hydrochloric acid, if necessary, gives, under similar circumstances, a crystalline yellow precipitate, which is a double salt of platinum tetrachloride and potassium chloride. Both this compound and cream of tartar are, however, soluble in about 60 parts of cold water. An addition of alcohol increases the delicacy of both tests.

(3.) *Perchloric acid*, and *silicofluoric acid*, give rise to slightly soluble white precipitates when added to a potassium-salt

(4.) Potassium salts usually colour the outer blow-pipe flame purple or violet; this reaction is clearly perceptible only when the potassium salts are pure.

(5.) The spectral phenomena exhibited by potassium compounds are mentioned at page 77.

SODIUM.

Atomic weight, 23. Symbol, Na (Natrium).

SODIUM is a very abundant element, and very widely diffused. It occurs in large quantities as chloride, in rock-salt, sea-water, salt-springs, and many other mineral waters; more rarely as carbonate, borate, and sulphate, in solution or in the solid state, and as silicate in many minerals.

Metallic sodium was obtained by Davy soon after the discovery of potassium, and by similar means. Gay-Lussac and Thénard afterwards prepared it by decomposing sodium hydroxide with metallic iron at a white heat; and Brunner showed that it may be prepared with much greater facility by distilling a mixture of sodium carbonate and charcoal.

The preparation of sodium by this last-mentioned process is much easier than that of potassium, not being complicated, or only to a slight extent, by the formation of secondary products. Within the last few years it has been considerably improved by Deville and others, and carried out on the manufacturing scale, sodium being now employed in considerable quantity as a reducing agent, especially in the manufacture of aluminium and magnesium, and in the silver amalgamation process.

The sodium carbonate used for the preparation is prepared by calcining the crystallised neutral carbonate. It must be thoroughly dried, then pounded, and mixed with a slight excess of pounded charcoal or coal. An inactive substance, viz., pounded chalk, is also added to keep the mixture in a pasty condition during the operation, and prevent the fused sodium carbonate from separating from the charcoal. The following are the proportions recommended by Deville:—

For Laboratory Operations.			*For Manufacturing Operations.*		
Dry sodium carbonate,	717	parts	Dry sodium carbonate,	30	kilogr.
Charcoal, . .	175	,,	Coal, . .	13	,,
Chalk, . .	108	,,	Chalk, . .	3	,,

These materials must be very intimately mixed by pounding and sifting, and it is advantageous to calcine the mixture before introducing it into the distilling apparatus, provided the calcination can be effected by the waste heat of a furnace; the mixture is thereby rendered more compact, so that a much larger quantity can be introduced into a vessel of given size.

The distillation is performed, on the laboratory scale, in a mercury bottle heated exactly in the manner described for the preparation of potassium. For manufacturing operations, the mixture is introduced into iron cylinders, which are heated in a reverberatory furnace, and so arranged that, at the end of the distillation, the exhausted charge may be withdrawn and a fresh charge introduced, without displacing the cylinders or putting out the fire. The receivers used in either case are the same in form and dimensions as those employed in the preparation of potassium (p. 317).

When the process goes on well, the sodium collected in the receivers is nearly pure; it may be completely purified by melting it under a thin layer of petroleum. This liquid is decanted as soon as the sodium becomes perfectly fluid, and the metal is run into moulds like those used for casting lead or zinc.

Sodium is a silver-white metal, greatly resembling potassium in every respect. Its specific gravity is 0·972. It is soft at common temperatures, melts at 97·6°, and oxidises very rapidly in the air. When placed on the surface of cold water, it decomposes that liquid with great violence, but seldom takes fire unless the motions of the fragment are restrained, and its rapid cooling is diminished by adding gum or starch to the water. With hot water it takes fire at once, burning with a bright yellow flame, and producing a solution of soda.

Sodium Chloride; Common Salt, NaCl.—This very important substance is found in many parts of the world in solid beds or irregular strata of immense thickness, as in Cheshire, Spain, Galicia, and many other localities. An inexhaustible supply exists also in the waters of the ocean, and large quantities are obtained from saline springs.

Rock-salt is almost always too impure for use. If no natural brine-spring exists, an artificial one is formed by sinking a shaft into the rock-salt, and, if necessary, introducing water. This when saturated is pumped up, and evaporated more or less rapidly in large iron pans. As the salt separates, it is removed from the bottom of the vessel by means of a scoop, pressed while still moist into moulds, and then transferred to the drying-stove. When large crystals are required, as for the coarse-grained *bay-salt* used in curing provisions, the evaporation is slowly conducted. Common salt is apt to be contaminated with magnesium chloride

Sodium chloride, when pure, is not deliquescent in moderately dry air. It crystallises in anhydrous cubes, which are often grouped together into pyramids, or steps. It requires about 2½ parts of water at 60° F. for solution, and its solubility is not sensibly increased by heat; it dissolves to some extent in spirit of wine, but is nearly insoluble in absolute alcohol. It melts at a red heat, and is volatile at a still higher temperature. The economical uses of common salt are well known.

The *iodide and bromide of sodium* much resemble the corresponding potassium-compounds: they crystallise in cubes, which are anhydrous, and very soluble in water.

Sodium Oxides.—Sodium forms a monoxide and a dioxide; also a hydroxide corresponding with the former.

Sodium Monoxide, or *Anhydrous Soda*, Na_2O, is produced, together with the dioxide, when sodium burns in the air, and may be obtained pure by exposing the dioxide to a very high temperature; or by heating sodium hydroxide with an equivalent quantity of sodium: $2NaHO + Na_2 = 2Na_2O + H_2$. It is a grey mass, which melts at a red heat, and volatilises with difficulty.

Sodium Hydroxide, or *Caustic Soda*, $NaHO$, or $Na_2O.H_2O$.—This substance is prepared by decomposing a somewhat dilute solution of sodium carbonate with calcium hydroxide: the description of the process employed in the case of potassium hydroxide, and the precautions necessary, apply word for word to that of sodium hydroxide.

The solid hydroxide is a white fusible substance, very similar in properties to potassium hydroxide. It is deliquescent, but dries up again after a time in consequence of the absorption of carbonic acid. The solution is highly alkaline, and a powerful solvent for animal matter: it is used in large quantity for making soap.

The strength of a solution of caustic soda may be roughly determined from a knowledge of its density, by the aid of the following table drawn up by Dalton:—

TABLE OF PERCENTAGE OF ANHYDROUS SODA, Na_2O, IN SOLUTIONS OF DIFFERENT DENSITY.

Density.	Percentage of anhydrous soda.	Density.	Percentage of anhydrous soda.
2·00	77·8	1·40	29·0
1·85	63·6	1·36	26·0
1·72	53·8	1·32	23·0
1·63	46·6	1·29	19·0
1·55	41·2	1·23	16·0
1·50	36·8	1·18	13·0
1·47	34·0	1·12	9·0
1·44	31·0	1·06	4·7

Sodium Dioxide, Na_2O_2.—Sodium, when heated to about 200° in a current of dry air, absorbs oxygen, and is converted into dioxide; this substance is white, but becomes yellow when heated, which tint it again loses on cooling. It dissolves in water without decomposition: the solution may be evaporated under the receiver of the air-pump, and, when sufficiently concentrated, deposits crystalline plates having the composition $Na_2O_2.8H_2O$. These crystals left to effloresce over oil of vitriol for nine days lose three-fourths of their water, and yield another hydrate containing $Na_2O_2 2H_2O$. The aqueous solution of sodium dioxide when heated on the water-bath, is decomposed into oxygen and the monoxide.

Sodium Nitrate, $NaNO_3$.—This salt, sometimes called *Cubic Nitre*, or *Chile Saltpetre*, occurs native, and in enormous quantity, at Tarapaca in Northern Peru, where it forms a regular bed, of great extent, along with gypsum, common salt, and remains of recent shells. The pure salt commonly crystallises in rhombohedrons, resembling those of calcareous spar. It is deliquescent, and very soluble in water. Sodium nitrate is employed for making nitric acid, but cannot be used for gunpowder, as the mixture burns too slowly, and becomes damp in the air. It has been lately used with some success in agriculture as a superficial manure or top-dressing; also for preparing potassium nitrate (p. 336).

Sodium Carbonates.—The *Neutral* or *Disodic Carbonate*, $Na_2CO_3.10H_2O$, was once exclusively obtained from the ashes of sea-weeds, and of plants, such as the *Salsola soda*, which grow by the sea-side, or, being cultivated in suitable localities for the purpose, are afterwards subjected to incineration. The *barilla*, still employed to a small extent in soap-making, is thus produced in several places on the coast of Spain, as at Alicante, Carthagena, &c. That made in Brittany is called *varec*.

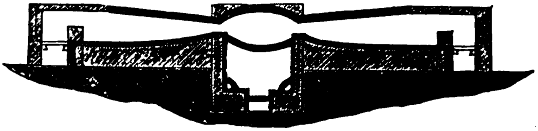
Sodium carbonate is now manufactured on a stupendous scale from common salt by a series of processes which may be divided into two stages:—

(1.) Manufacture of sodium sulphate, or salt-cake, from sodium chloride (common salt); this is called the salt-cake process.

(2.) Manufacture of sodium carbonate, or soda-ash; called the soda-ash process.

(1.) *Salt-cake process.*—This process consists in the decomposition of common salt by sulphuric acid, and is effected in a furnace called the *Salt-cake furnace*, of which fig. 144 represents a section. It consists of a large covered iron pan, placed in the centre, and heated by a fire underneath; and two roasters, or reverberatory furnaces, placed one at each end, and on the hearths of which the salt is com-

Fig. 144.



pletely decomposed. The charge of half a ton of salt is first placed in the iron pan, and then the requisite quantity of sulphuric acid is allowed to pass in upon it. Hydrochloric acid is evolved, and escapes through a flue, with the products of combustion, into towers or scrubbers, filled with coke and bricks moistened with a stream of water; the acid vapours are thus condensed, and the smoke and heated air pass up the chimney. After the mixture of salt and acid has been heated in the iron pan, it becomes converted into a solid mass of acid sodium sulphate and undecomposed sodium chloride:—

$$2NaCl + H_2SO_4 = NaCl + NaHSO_4 + HCl.$$

It is then raked on to the hearths of the furnaces at each side of the decomposing pan, where the flame and heated air of the fire complete the decomposition into neutral sodium sulphate and hydrochloric acid:—

$$NaCl + NaHSO_4 = Na_2SO_4 + HCl.$$

(2) *Soda-ash process.*—The sulphate is next reduced to powder, and mixed with an equal weight of chalk or limestone, and half as much small coal, both ground or crushed. The mixture is thrown into a reverberatory furnace, and heated to fusion, with constant stirring. When the decomposition is judged complete, the melted matter is raked from the furnace into an iron trough, where it is allowed to cool. This crude product, called *black ash* or *ball-soda,* is broken up into little pieces, when cold, and lixiviated with cold or tepid water. The solution is evaporated to dryness, and the salt calcined with a little sawdust in a suitable furnace. The product is the *soda ash* or *British alkali* of commerce, which, when of good quality, contains from 48 to 52 per cent. of anhydrous soda, Na_2O, partly in the state of carbonate, and partly as hydroxide, the remainder being chiefly sodium sulphate and common salt, with occasional traces of sulphite or thiosulphate, and also cyanide of sodium. By dissolving soda-ash in hot water, filtering the solution, and then allowing it to cool slowly, the carbonate is deposited in large transparent crystals.

The reaction which takes place in the calcination of the sulphate with chalk and coal-dust seems to consist, first, in the conversion of the sodium sulphate into sulphide by the aid of the combustible matter, and, secondly, in the interchange of elements between that substance and the calcium carbonate:

$$Na_2S + CaCO_3 = CaS + Na_2CO_3.$$

Several other processes for the manufacture of soda have been devised and even carried into execution, but the only one which appears to hold out any prospect of commercial success is that which is called the "ammonia soda-process."* This method, first suggested about forty years ago, has been tried at several works in England and in Germany. It consists in decomposing a solution of common salts with ammonium bicarbonate, whereby the greater part of the sodium is precipitated as bicarbonate, while the ammonia remains in solution as ammonium chloride. This latter salt is heated with lime to liberate ammonia, which is then reconverted into bicarbonate by the carbonic acid evolved in the conversion of the sodium bicarbonate into monocarbonate by heat; and the ammonium bicarbonate thus reproduced is employed to decompose fresh portions of sodium chloride, so that the process is made continuous. The chief advantages claimed for this process are the direct conversion of the sodium chloride into carbonate, which is precipitated from the concentrated liquors uncontaminated with salts of other metals; the absolute freedom of the product from sulphur-compounds; and lastly, simplicity of plant, saving of fuel, and freedom from noxious vapours and troublesome secondary products.

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* Chemisches Centralblatt, 1873, p. 636; 1874, pp. 274, 370, 502.

The chief obstacle to its profitable employment appears to be that, with certain proportions of the materials, and under certain conditions of temperature and concentration, a reverse reaction takes place, whereby the sodium bicarbonate and ammonium chloride are reconverted into ammonium carbonate and sodium chloride.

The ordinary crystals of sodium carbonate contain ten molecules of water; but by particular management the same salt may be obtained with fifteen, nine, seven molecules, or sometimes with only one. The common form of the crystals is derived from an oblique rhombic prism; they effloresce in dry air, and crumble to a white powder. Heated, they fuse in their water of crystallisation; when the latter has been expelled, and the dry salt exposed to a full red heat, it melts without undergoing change. The common crystals dissolve in two parts of cold, and in less than their own weight of boiling water: the solution has a strong, disagreeable, alkaline taste, and a powerfully alkaline reaction.

Hydrogen and Sodium Carbonate, Hydrosodic Carbonate, Monosodic Carbonate, Acid Sodium Carbonate, $NaHCO_3$ or $Na_2CO_3.H_2CO_3$, commonly called *Bicarbonate of soda.*—This salt is prepared by passing carbonic acid gas into a cold solution of the neutral carbonate, or by placing the crystals in an atmosphere of the gas, which is rapidly absorbed, while the crystals lose the greater part of their water, and pass into the new compound.

Monosodic carbonate, prepared by either process, is a crystalline white powder, which cannot be re-dissolved in warm water without partial decomposition. It requires 10 parts of water at 15·5° for solution: the liquid is feebly alkaline to test-paper, and has a much milder taste than that of the neutral carbonate. It does not precipitate a solution of magnesia. By exposure to heat, the salt is converted into neutral carbonate.

Dihydro-tetrasodic Carbonate, $Na_4H_2(CO_3)_3.2H_2O$.—This salt, commonly called *sesquicarbonate of soda,* may be regarded as a compound of the neutral and acid salts ($Na_2CO_3.2NaHCO_3$).

It occurs native on the banks of the soda lakes of Sokenna, near Fezzan, in Africa, where it is called *tronai;* also as *urao,* at the bottom of a lake in Maracaibo, South America. It is produced artificially, though with some difficulty, by mixing the monosodic and diosodic carbonates in the proportions above indicated, melting them together, drying, and exposing the dried mass in a cellar for some weeks; it then absorbs water, becomes crystalline, and contains spaces filled with the tetrasodic carbonate.

Sodium and *Potassium Carbonate,* $NaKCO_3.6H_2O$, separates in monoclinic crystals from a solution containing the two carbonates in equivalent proportions.

A mixture of these two carbonates in equivalent proportions melts at a much lower heat than either of the salts separately; such a mixture is very useful in the fusion of silicates, &c.

Alkalimetry.—Analysis of Alkaline Hydroxides and Carbonates.

The amount of alkali or alkaline carbonate in commercial potash soda, or ammonia, is estimated by determining the quantity of an acid of given strength required to neutralise a given weight of the sample. The estimation depends upon the facts that the alkaline salts of strong acids (sulphuric, oxalic, &c.) are neutral to litmus: and that the violet solution of litmus is coloured blue by caustic alkalis or alkaline carbonates, wine-red by carbonic acid, and light red by strong acids.

The first step is the preparation of the standard acid. It is best to make this liquid of such strength that 1000 cubic centimeters (1 litre) shall contain exactly one ½ *gram-molecule* (*i.e.,* 1 molecule expressed in ½ grams) of the acid.

About 70 grams of concentrated sulphuric acid are diluted with about 600 grams of water; when the mixture is cool, the volume of it necessary to saturate 5·3 grams (one ½ decigram-molecule) of pure anhydrous sodium carbonate, Na_2CO_3, is determined.* For this purpose 5·3 grams of freshly ignited sodium carbonate are dissolved in hot water, the solution coloured blue with a few drops of litmus, and the acid added from a burette or alkalimèter (p. 351), at last drop by drop, till the colour just passes from wine-red to light red, and till strips of litmus-paper, moistened with the solution, begin to retain the colour when dry. The volume of acid employed is then noted, and the whole diluted so as to approximate to the required strength. Suppose, for instance, 37 cubic centimeters of acid have been used: water is then added till every 100 volumes is diluted to 250 volumes, and another determination is made. If 90 cubic centimeters are now required to saturate the ½ decigram alkaline solution, every 90 volumes of the acid must be diluted to 100, and the result controlled by a fresh determination; 100 cubic centimeters of this acid should exactly saturate 5·3 grams of sodium carbonate, and will contain 1 half-decigram-molecule of acid; 2 cubic centimeters will therefore contain 1 milligram-molecule (0·098 gram),* and will saturate 2 milligram-molecules of an alkali (KHO or NaHO), or 1 milligram-molecule of an alkaline carbonate (K_2CO_3 or Na_2CO_3).

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* The molecule of sodium carbonate, Na_2CO_3, weighs $2.23+12+3.16=106$.

To estimate the proportion of alkali in a commercial sample, a weighed portion of the substance is dissolved in water (if a solid); a few drops of litmus are added; the standard acid is added from a burette, until the first permanent appearance of a light red colour; and the volume of acid employed is read off. Each cubic centimeter of acid corresponds to 1 milligram-molecule of alkali, or 1 half milligram-molecule of alkaline carbonate; *i.e.*, to 0.053 gram of sodium carbonate, Na_2CO_3, 0·069 gram potassium carbonate, K_2CO_3, 0·040 gram of caustic soda, NaHO, 0·056 gram of caustic potash, KHO, and 0·017 gram of ammonia, NH_3; and a simple proportion gives the amount of alkali or alkaline carbonate present (*e.g.*, 100 : 6·9 : : number of cubic centimeters employed : potassium carbonate present). By operating on 100 times the $\frac{1}{2}$ milligram-molecule *e.g.*, 6·9 grams in the case of potassium carbonate, 5·3 grams in the case of sodium carbonate) all calulation is saved : for as this amount, if present, would require 100 cubic centimeters of acid for its saturation, the number of cubic centimeters actually required at once indicates the percentage of alkaline carbonate. The burettes commonly used contain 50 cubic centimeters, and are graduated into half cubic centimeters; so that by operating on 50 times the $\frac{1}{2}$ milligram-moleule, the number of divisions employed indicates the percentage.

Sometimes, instead of exactly neutralising the alkali with the standard acid, it is better to add the acid till the litmus assumes a distinct light red colour, then heat the solution to boiling, and add a small excess (5 to 10 cubic centimeters) of acid. The hot solution is freed from carbonic acid by agitation and by drawing air through it with a glass tube; and then neutralised with a standard solution of caustic soda (100 cubic centimeters of which exactly saturate 100 cubic centimeters of the standard acid) till the colour just changes from red to blue. Since the acid and alkaline solutions neutralise each other volume for volume, it is only necessary to deduct the number of cubic centimeters employed of the latter from that of the former, and calculate the amount of alkali from the residue. This method, called the *indirect* or *residual method*, is preferable to the direct method previously described for the analysis of carbonates, since the change from blue to red is more distinctly marked than that from one shade of red to another.

The standard solution of caustic soda must be kept in a flask, into the cork of which is inserted a calcium chloride tube filled with a mixture of sodium sulphate and quicklime, which effectually prevents the absorption of carbonic acid. If the burette be closed with a similar tube, the soda-solution may remain in it for days.

The "alkalimeter" or "burette" is a glass tube (fig. 145) closed at one end and moulded into a spout or lip at the other, and marked with any convenient scale of equal parts generally, as above mentioned, into 100 half cubic centimeters.* A strip of paper is pasted on the tube and suffered to dry, after which the instrument is graduated by counterpoising it in a nearly upright position in the pan of a balance of moderate delicacy, and weighing into it, in succession, 5, 10, 15, 20, &c., grams of distilled water at 4° C. until the whole quantity, amounting to 50 grams (50 cubic centimeters), has been introduced, the level of the water in the tube being, after each addition, carefully marked with a pen upon the strip of paper, while the tube is held quite upright, and the mark made between the top and bottom of the curve formed by the surface of the water. The smaller divisions of the scale, of a half cubic centimeter each, may then be made by dividing with compasses each of the spaces into ten equal parts. When the graduation is complete, and the operator is satisfied with its accuracy, the marks may be transferred to the tube itself by a sharp file, and the paper removed by a little warm water. The numbers are scratched on the glass with the hard end of the same file, or with a diamond. Or the glass is covered with etching wax, the scale traced upon it with a fine needle point, and the marks etched by exposing the tube to the vapour of hydrofluoric acid.

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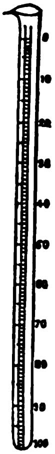
* The molecular weight of sulphuric acid, H_2SO_4, is 98 = 2 + 32 + 4 . 16.

Fig. 145.



The alkalimeter, represented in fig. 145, is the simplest form of this instrument. The pouring out of minute quantities is, however, greatly facilitated by providing the measure with a narrow dropping tube, fig. 146, the lower extremity of which is soldered into the measure, whilst the upper one is bent outward and sharply cut off. This kind of burette, which is known as Gay-Lussac's, is chiefly used in France. The liquid may be very conveniently poured from it; but it is rather easily broken, so that its manipulation requires a good deal of care. This defect is greatly obviated in the burette, fig. 147, in which the graduated tube is provided with a spout at the top, there being at the same time an orifice for pouring in the liquid.

A very elegant instrument has been contrived by Dr. Mohr of Coblentz. It is a graduated tube, drawn out at one end to a point, to which is attached, by means of a narrow vulcanised caoutchouc tube, a short glass tube, likewise drawn out to a point (fig. 148). There is a small space (about ½ inch) between the two tubes, upon which is fixed a metallic clamp, *a*, represented in its actual dimensions in fig. 149. This clamp shuts off the connection between the graduated cylinder and the small glass tube. But by pressing with the fingers upon the ends *b b*, of this clamp, it opens, and allows the liquid to flow out of the lower tube. It is evident that by this arrangement the amount of liquid may be regulated with the greatest nicety.

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* It may also be divided into 1000 grain-measures, the grain-measure being the capacity of a grain of distilled water at 60° F.; 70,000 such measures go to an imperial gallon, and 8750 to a pint.

Fig. 146.

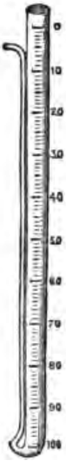


Fig. 147.

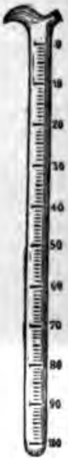


Fig. 148.

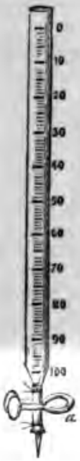
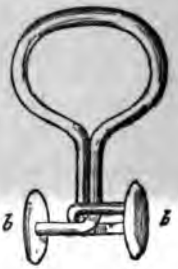
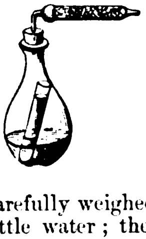


Fig. 149.



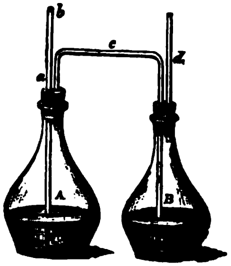
It is often desirable, in the analysis of carbonates, to determine directly the proportion of carbonic acid: the following methods give very exact results:—

Fig. 150.



A small light glass flask of three or four ounces capacity, with lipped edge, is chosen, and a cork fitted to it. A piece of tube about three inches long is drawn out at one extremity, and fitted, by means of a small cork and a bit of bent tube, to the cork of the flask. This tube is filled with fragments of calcium chloride, prevented from escaping by a little cotton at either end: the joints are secured by sealing wax. A short tube, closed at one extremity, and small enough to go into the flask, is also provided, and the apparatus is complete. Fifty grains of the carbonate to be examined are carefully weighed out and introduced into the flask, together with a little water; the small tube is then filled with oil of vitriol, and placed in the flask in a nearly upright position, and leaning against its sides in such a manner that the acid does not escape. The cork and calcium chloride tube are then adjusted, and the whole apparatus *is accurately* counterpoised on the balance. This done, the flask is slightly inclined, so that the oil of vitriol may slowly mix with the other substances and decompose the carbonate, the gas from which escapes in a dry state from the extremity of the tube. When the action has entirely ceased, the liquid is heated until it boils, and the steam begins to condense in the drying tube; it is then left to cool, and weighed, when the loss indicates the quantity of carbon dioxide The acid must be in excess after the experiment. When calcium carbonate is thus analysed, hydrochloric acid must be substituted for the sulphuric acid.

Fig. 151.



Instead of the above apparatus, a neat arrangement may be used, which was first suggested by Will and Fresenius. It consists of two small glass flasks, A and B, the latter being somewhat smaller than the former. Each of the flasks is provided with a doubly perforated cork. A tube, open at both ends, but closed at the upper extremity by means of a small quantity of wax, passes through the cork of A to the very bottom of the flask, whilst a second tube, reaching to the bottom of B, establishes a communication between the two flasks. The cork of B is provided, moreover, with a short tube, *d*. In order to analyse a carbonate, a suitable quantity (fifty grains) is put into A, together with some water. B is half filled with concentrated sulphuric acid, the apparatus tightly fitted and weighed. A small quantity of air is now sucked out of flask B by means of the tube *d*, whereby the air in A is likewise rarefied. On allowing the air to return, a quantity of the sulphuric acid ascends to the tube *c*, and flows over into flask A, causing a disengagement of carbon dioxide, which escapes at *d*, after having been perfectly dried by passing through the bottle B. This operation is repeated until the whole of the carbonate is decomposed, and the process is terminated by opening the wax stopper, and drawing a quantity of air through the apparatus. The apparatus is now reweighed. The difference of the two weighings expresses the quantity of carbon dioxide in the compound analysed.

Sodium Sulphate, $Na_2SO_4.10H_2O$, commonly called *Glauber's salt*, is a by-product in several chemical operations and an intermediate product in the manufacture of the carbonate as above described: it may of course be prepared directly, if wanted pure, by adding dilute sulphuric acid, to saturation, to a solution of sodium carbonate. It crystallises in forms derived from an oblique rhombic prism: the crystals contain 10 molecules of water, are efflorescent, and undergo watery fusion when heated, like those of the carbonate: they are soluble in twice their weight of cold water, and rapidly increase in solubility as the temperature of the liquid rises to 33°, at which contain it, as that at Cheltenham

Sodium and Hydrogen Sulphate, or
$2NaHSO_4.3H_2O$ or $Na_2SO_4.H_2SO_4.3H_2O$, co
of soda, is prepared by adding to 10 parts
sulphate, 7 of oil of vitriol, evaporating th
gently igniting. The acid sulphate is very
an acid reaction. It is not deliquescent.
heated, the fused salt gives up anhydro
becomes neutral sulphate; a change which
previous formation of a pyrosulphate, Na_2S_2

Sodium Hyposulphite, Na_2SO_2.—This
deoxidising action of zinc on the sulphite, N
has already been described (p. 213). It
soluble in water and in weak spirit, the sol
bleaching and reducing properties. The
to the air in the moist state, rapidly beco
a property by which this salt is distinguis
phate.

Sodium Thiosulphate, $Na_2S_2O_3$, forme
This salt is formed from the sulphite, Na_2SO_3,
There are several modes of procuring it. On
neutral *sodium sulphite*, by passing a strea
phurous oxide gas into a strong solution of
then digesting the solution with sulphur a
several days. By careful evaporation at a
the salt is obtained in large regular crystals,
in water. It is used in considerable quan
purposes, and as an antichlore.

alkaline to test-paper. Crystals containing 7 molecules of water, and having a form different from that above mentioned, have been obtained.

A *trisodic orthophosphate*, sometimes called *subphosphate*, $Na_3PO_4.12H_2O$, is obtained by adding a solution of caustic soda to the preceding salt. The crystals are slender six-sided prisms, soluble in five parts of cold water. It is decomposed by acids, even carbonic, but suffers no change by heat, except the loss of its water of crystallisation. Its solution is strongly alkaline. *Monosodic orthophosphate*, $NaH_2PO_4.H_2O$, often called superphosphate or biphosphate, may be obtained by adding phosphoric acid to the ordinary phosphate, until it ceases to precipitate barium chloride, and exposing the concentrated solution to cold. The crystals are prismatic, very soluble, and have an acid reaction. When strongly heated, this salt becomes changed into monobasic sodium phosphate, or metaphosphate.

Sodium, Ammonium, and Hydrogen Phosphate; Phosphorus Salt; Microcosmic Salt, $Na(NH_4)HPO_4.4H_2O$.—Six parts of common sodium phosphate are heated with 2 parts of water, until the whole is liquefied, and one part of powdered sal-ammoniac is added; common salt then separates, and may be removed by a filter; and from the solution, duly concentrated, the microcosmic salt is deposited in prismatic crystals, which may be purified by one or two re-crystallisations. Microcosmic salt is very soluble. When gently heated, it parts with its 4 molecules of crystallisation-water, and, at a higher temperature, the basic hydrogen is likewise expelled as water, together with ammonia, and a very fusible compound, sodium metaphosphate, remains, which is valuable as a flux in blow-pipe experiments. Microcosmic salt occurs in decomposed urine.

Tetrasodic Phosphate, or *Sodium Pyrophosphate*, $Na_4P_2O_7.10H_2O$, is prepared by strongly heating common disodic orthophosphate, dissolving the residue in water, and recrystallising. The crystals are very brilliant, permanent in the air, and less soluble than the original phosphate: their solution is alkaline. A *sodiohydric pyrophosphate* has been obtained; but it does not crystallise.

Monosodic Phosphate, or *Sodium Metaphosphate*, $NaPO_3$, is obtained by heating either the acid tribasic phosphate, or microcosmic salt. It is a transparent glassy substance, fusible at a dull red heat, deliquescent, and very soluble in water. It refuses to crystallise, but dries up into a gum-like mass.

If this glassy phosphate be cooled very slowly, it separates as a beautiful crystalline mass. It may be purified by means of boiling water from the vitreous metaphosphate, which will not crystallise. Another metaphosphate has been obtained by adding sodium sulphate to an excess of phosphoric acid, evaporating, and heating to upwards of 315°. Possibly these several metaphosphates may be represented by the formulæ $NaPO_3$, $Na_2P_2O_6$, and $Na_3P_3O_9$.

The tribasic phosphates, or orthophosphates, give a bright yellow precipitate with solution of silver nitrate; the bibasic and monobasic

in equivalent proportions, and dissolving
forms large crystals containing $NaBO_2.3H_2O$.

The *Anhydroborate*, *Biborate*, or *Borax*, 2N
$Na_2O.2B_2O_3.10H_2O$, occurs in the waters of certa
and Persia: it is imported in a crude state fro
name of *tincal*. When purified it constitutes the
Much borax is now, however, manufactured fro
acid of Tuscany, also from a native calcium bo
which occurs in southern Peru. Borax cryst
prisms, which effloresce in dry air, and require 2
6 of boiling water for solution. On exposing
molecules of water of crystallisation are expelle
temperature the salt fuses, and assumes a gl
cooling: in this state it is much used for blow-pi
metallic oxides dissolving in it to transparent be
are distinguished by characteristic colours. By
ment, crystals of borax can be obtained with 5
they are very hard, and permanent in the air.
constitution an acid salt, has an alkaline reactic
is used in the arts for soldering metals, its a
rendering the surfaces to be joined metallic, by di
and it sometimes enters into the composition
which stoneware is covered.

Sodium Sulphide, Na_2S, is prepared in th
potassium monosulphide; it separates from a c
in octohedral crystals, which are rapidly dec
with the air into a mixture of sodium hydrate a
forms double sulphur salts with hydrogen sulphid
and other sulphur acids.

Sodium sulphide is supposed to enter into the

There is no good precipitant for sodium, all its salts being very soluble, with the exception of the *metantimonate*, which is precipitated on mixing a solution of a sodium salt with a solution of potassium metantimonate; the use of this reagent is, however, attended with some difficulties. The presence of sodium is often determined by negative evidence. The yellow colour imparted by sodium salts to the outer flame of the blow-pipe, and to combustible matter, is a character of considerable importance. The spectral phenomena exhibited by sodium compounds are mentioned on page 77.

AMMONIUM.

The ammonia salts are most conveniently studied in this place, on account of their close analogy to those of potassium and sodium. These salts are formed by the direct union of ammonia, NH_3, with acids, and as already pointed out (p. 164), they may be regarded as compounds of acid radicles, Cl, NO_3, SO_4, &c., with a basylous radicle, NH_4, called ammonium, which plays in these salts the same part as potassium and sodium in their respective compounds; thus:—

$$\underset{\text{Ammonia.}}{NH_3} + \underset{\text{Hydrochloric acid.}}{HCl} = \underset{\text{Ammonium chloride.}}{NH_4.Cl}$$

$$NH_3 + \underset{\text{Nitric acid.}}{HNO_3} = \underset{\text{Ammonium nitrate.}}{NH_4.NO_3}$$

$$NH_3 + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Acid ammonium sulphate.}}{NH_4.H.SO_4}$$

$$2NH_3 + H_2SO_4 = \underset{\text{Neutral ammonium sulphate.}}{(NH_4)_2.SO_4}.$$

The radicle NH_4 is not capable of existing in the free state, inasmuch as it contains an uneven number of monad atoms: it is simply the residue which is left on removing the atom of chlorine from the saturated molecule, NH_4Cl. Whether the double molecule N_2H_8, or

$$\begin{array}{c}NH_4\\ |\\ NH_4\end{array}$$

, has a separate existence, is a different question. Ammonium is said, indeed, to be capable of forming an amalgam with mercury; but even in this state it is quickly resolved into ammonia and free hydrogen.

When a globule of mercury is placed on a piece of moistened potassium hydroxide, and connected with the negative side of a voltaic battery of very moderate power, the circuit being completed through

attended by heat and light. When cold, the
into a capsule, and covered with a strong soluti
The production of an ammoniacal amalgam i
the mercury increasing prodigiously in volume,
pasty. The increase of weight is, however, qui
from $\frac{1}{1800}$ to $\frac{1}{1200}$ part. Left to itself, the amalgam
into fluid mercury, ammonia, and hydrogen.
indeed, that the so-called amalgam may be
mercury which has absorbed a certain quantity
as silver, when heated to a very high tempe
taking up about twenty times its volume of
gives up again on cooling.*

But whether ammonium has any separate e
quite certain that many ammoniacal salts ar
those of potassium ; and if from any two of th
as the nitrates, KNO_3 and NH_4NO_3, we subtr
common to the two, there remain the metal K
which are, therefore, supposed to be isomorpho

Ammonium Chloride, Sal-ammoniac, N
Sal-ammoniac was formerly obtained from Egy
sublimation from the soot of camels' dung : it
factured from the ammoniacal liquid of the gas
condensed products of the distillation of bon
refuse, in the preparation of animal charcoal.

These impure and highly offensive solutio
slight excess of hydrochloric acid, by whic
neutralised, and the carbonate and sulphide
evolution of carbonic acid and sulphuretted h
liquid is evaporated to dryness, and the salt car
[illegible] the tarry matter ; it is then puri

hot water. By heat, it is sublimed without decomposition. The crystals are anhydrous. Ammonium chloride forms double salts with the chlorides of magnesium, nickel, cobalt, manganese, zinc, and copper.

Ammonium Nitrate, $(NH_4)NO_3$, is easily prepared by adding ammonium carbonate to slightly diluted nitric acid until neutralisation has been reached. By slow evaporation at a moderate temperature it crystallises in six-sided prisms, like those of potassium nitrate ; but, as usually prepared for making nitrogen monoxide, by quick boiling until a portion solidifies completely on cooling, it forms a fibrous and indistinct crystalline mass.

Ammonium nitrate dissolves in two parts of cold water, producing considerable depression of temperature; it is but feebly deliquescent, and deflagrates like nitre on contact with heated combustible matter. Its decomposition by heat has been already explained (p. 159).

Ammonium Sulphate, $(NH_4)_2SO_4$.—Prepared by neutralising ammonium carbonate with sulphuric acid, or on a large scale, for use as a manure, by adding sulphuric acid in excess to the coal-gas liquor just mentioned, and purifying the product by suitable means. It is soluble in 2 parts of cold water, and crystallises in long, flattened, six-sided prisms. It is entirely decomposed and driven off by ignition, and, even to a certain extent, by long boiling with water, ammonia being expelled and the liquid rendered acid.

Ammonium Carbonates.—There are three definite carbonates of ammonia, the composition of which is as follows :—

Normal or diammonic carbonate,	$(NH_4)_2CO_3.H_2O$
Acid or ammonio-hydric carbonate,	$(NH_4)HCO_3$
Half-acid, or tetrammonio-dihydric carbonate,	$(NH_4)_4H_2(CO_3)_3.H_2O$.

(1.) The *normal carbonate* is prepared by addition of ammonia to one of the acid salts, or of water to the carbamate of ammonia, CON_2H_6 (p. 362), with certain special precautions, the description of which is too long for insertion in this work, to prevent the escape of a portion of the ammonia. It crystallises in elongated plates or flattened prisms, having a caustic taste, a powerful ammoniacal odour, and easily giving off ammonia and water, whereby they are converted into the acid carbonate :

$$(NH_4)_2CO_3.H_2O = NH_3 + H_2O + (NH_4)HCO_3.$$

(2.) *Ammonium and Hydrogen Carbonate,* or *Mono-ammonic Carbonate,* $(NH_4)HCO_3$, commonly called *Bicarbonate,* or *Acid*

verted into mono-ammonic carbonate. This sa
belonging to the trimetric system. Accor
dimorphous, but never isomorphous with mo
when exposed to the air, it volatilises slowly
ammoniacal odour. It dissolves in 8 parts of co
decomposing gradually at ordinary tempera
heated above 30°, with evolution of ammoni
alcohol, but when exposed to the air, under a
normal carbonate, evolving carbon dioxide.

It has been found native in considerable qua
guano on the western coast of Patagonia, in wh
having a strong ammoniacal odour.

(3.) *Tetrammonio-dihydric Carbonate*, $N_4H_{18}C_3$
—This salt, also called *half-acid carbonate*
ammonia, contains the elements of 1 molecule
molecules of mono-ammonic carbonate, into
resolved by treatment with water or alcohol:

$$(NH_4)_4H_2(CO_3)_3 = (NH_4)_2CO_3 + 2($$

It is obtained by dissolving the commercial
aqueous ammonia, at about 30°, and crystallisi
forms large transparent rectangular prisms, ha
truncated by octohedral faces. These cryst
rapidly in the air, giving off water and ammo
verted into mono-ammonic carbonate.

Commercial carbonate of ammonia (*sal volati*
consists of half acid carbonate more or less mix
It is prepared on the large scale by the dry d
hartshorn, and other animal matter, and is pu

Ammonium Sulphides.—Several of these compounds exist, and may be formed by distilling with sal-ammoniac the corresponding sulphides of potassium or sodium.

Ammonium and Hydrogen Sulphide, or *Ammonium Hydrosulphide*, $(NH)_4HS$, is a compound of great practical utility; it is obtained by saturating a solution of ammonia with well-washed sulphuretted hydrogen gas, until no more of the latter is absorbed. The solution is nearly colourless at first, but becomes yellow after a time, without, however, suffering material injury, unless it has been exposed to the air. It gives precipitates with most metallic solutions, which are very often characteristic, and is of great service in analytical chemistry.

Ammoniacal salts are easily recognised; they are all decomposed or volatilised at a high temperature; and when heated with calcium hydroxide or solution of alkaline carbonate, they give off ammonia, which may be recognised by its odour and alkaline reaction. The salts are all more or less soluble, the acid tartrate and the platinochloride being, however, among the least soluble: hence ammonium salts cannot be distinguished from potassium salts by the tests of tartaric acid and platinum solution. When a solution containing an ammoniacal salt, or free ammonia, is mixed with potash, and a solution of *mercuric iodide* in *potassium iodide* is added, a brown precipitate or coloration is immediately produced, consisting of dimercurammonium iodide, NHg_2I:

$$NH_3 + 2HgI_2 = NHg_2I + 3HI.$$

This is called Nessler's test; it is by far the most delicate test for ammonia that is known.

Amic Acids and Amides.

Sulphamic Acid.—When dry ammonia gas is passed over a thin layer of sulphuric oxide, SO_3, the gas is absorbed, and a white crystalline powder is formed, having the composition $N_2H_6SO_3$, that is, of ammonium sulphate minus one molecule of water:—

$$N_2H_6SO_3 = (NH_4)_2SO_4 - H_2O.$$

It is not, however, a salt of sulphuric acid: for its aqueous solution does not give any precipitate with baryta-water or soluble barium salts. It is, in fact, the ammonium salt of sulphamic acid, an acid derived from sulphuric acid, SO_4H_2 or $SO_2(HO)_2$, by substitution of the univalent radicle, NH_2 (p. 263), for one atom of hydroxyl, HO. The formula of this acid is $SO_2(NH_2)H$, and that of its ammonium salt, $SO_3(NH_2)NH_4$, or $SO_3N_2H_6$. Ammonium sulphamate is permanent in the air, and dissolves without decomposition in water. Its solution evaporated in a vacuum, over oil of vitriol, yields the salt in transparent colourless crystals.

The solution of the ammonium salt, mixed with baryta-water, gives off ammonia, and yields a solution of *barium sulphamate* $(SO_3NH_2)_2Ba$, which may be obtained by evaporation in well-defined crystals; and the solution of this salt, decomposed with potassium sulphate, yields *potassium sulphamate*, $SO_3(NH_2)K$.

Carbamic Acid.—When dry ammonia gas is mixed with carbon dioxide, the mixture being kept cool, the gases combine in the proportion of 2 volumes of the former to 1 volume of the latter, forming a pungent, very volatile substance, which condenses in white flocks. This substance has the composition $CO_2N_2H_6$, that is, of normal ammonium carbonate, $CO_3(NH_4)_2$, *minus* one molecule of water. It exists, as already observed, in commercial carbonate of ammonia (p. 360). It was formerly called *anhydrous carbonate of ammonia;* but, like the preceding salt, it is not really a carbonate, but the ammonium salt of carbamic acid, $CO_2(NH)_2H$, an acid derived from carbonic acid, CO_3H_2 or $CO(OH)_2$, by substitution of amidogen, NH_2, for 1 atom of hydroxyl. Ammonium carbamate dissolves readily in water, and quickly takes up one molecule of that compound, whereby it is converted into normal ammonium carbonate. When treated with sulphuric oxide, it is converted into ammonium sulphamate.

Carbamide, CON_2H_4.—When ammonia gas is mixed with carbon oxychloride or phosgene gas, $COCl_2$, a white crystalline powder is formed, having this composition:—

$$COCl_2 + 2NH_3 = 2HCl + CON_2H_4.$$

This compound, which is likewise formed in other reactions to be afterwards considered, is derived from carbonic acid, $CO(OH)_2$, by substitution of 2 atoms of amidogen for 2 atoms of hydroxyl. It differs from carbamic acid in being a neutral substance, not containing any hydrogen easily replaceable by metals.

Other bibasic acids likewise yield an amic acid and a neutral amide by substitution of 1 or 2 atoms of amidogen for hydroxyl. Tribasic acids yield in like manner two amic acids and one neutral amide, and tetrabasic acids may yield three amic acids and a neutral amide; thus, from pyrophosphoric acid, $P_2O_7H_4 = P_2O_3(HO)_4$, are obtained the three amic acids $P_2O_6(NH_2)H_3$, $P_2O_5(NH_2)_2H_2$, and $P_2O_4(NH_2)_3H$.

Monobasic acids, which contain but one atom of hydroxyl, yield by this mode of substitution only neutral amides, no amic acids: thus, from acetic acid, $C_2H_4O_2 = C_2H_3O.HO$, is obtained acetamide, $C_2H_3O(NH_2)$.

The neutral amides may also be regarded as derived from one or more molecules of ammonia, by substitution of univalent or multivalent acid radicles, for hydrogen: thus, acetamide $= NH_2(C_2H_3O)$; *carbamide*, $N_2H_4(CO)''$, &c.

By similar substitution of metals, or basylous compound radicles for the hydrogen of ammonia, basic compounds, called amines, are formed. Thus, when potassium is gently heated in ammonia gas, *monopotassamine*, NH_2K, is formed. It is an olive-green substance, which is decomposed by water into ammonia and potassium hydroxide :—

$$NH_2K + H_2O = NH_3 + KHO.$$

It melts at a little below 100, and when heated in a close vessel, is resolved into ammonia and *tripotassamine*:—

$$3NH_2K = 2NH_3 + NK_3.$$

The latter effervesces violently with water, yielding ammonia and potassium hydroxide :—

$$NK_3 + 3H_2O = NH_3 + 3KHO.$$

The formation and properties of amides and amines will be further considered under Organic Chemistry.

Metallammoniums.—These are hypothetical radicles derived from ammonium, N_2H_8, by substitution of metals for hydrogen. Salts of such radicles are formed in several ways. Ammonia gas is absorbed by various metallic salts in different proportions, forming compounds, some of which may be formulated as salts of metallammoniums. Thus, platinum dichloride, $PtCl_2$, absorbs two molecules of ammonia, forming *platosammonium chloride*, $N_2H_6Pt''.Cl_2$, and platinum tetrachloride, $Pt^{iv}Cl_4$, absorbs four molecules of ammonia, forming *platinammonium chloride*, $N_4H_{12}Pt^{iv}.Cl_4$. In like manner, cupric chloride and sulphate form the *chloride* and *sulphate of cuprammonium*, $N_2H_6Cu''.Cl_2$ and $N_2H_6Cu''.SO_4$.

Similar compounds are formed in many cases by precipitating metallic salts with ammonia or ammoniacal salts : thus, ammonia added to a solution of mercuric chloride, $HgCl_2$, forms a white precipitate, consisting of *dimercurammonium chloride*, $N_2H_4Hg''_2.Cl_2$; and by dropping solution of mercuric chloride into a boiling solution of sal-ammoniac mixed with free ammonia, crystals are obtained, consisting of *mercurammonium chloride*, $N_2H_6Hg''.Cl_2$. Some of these compounds will be further considered in connection with the several metals.

times occu
in mineral springs. The most abundant sou
is the mineral water of Wheal Clifford in
exists to the amount of 61 parts in a million.

The metal is obtained by fusing pure lithi
thick porcelain crucible, and decomposing t
electricity. It is a white metal like sodium,
Lithium fuses at 180° ; its specific gravity is
the lightest solid known.

A lithium salt may be obtained from petali
by the following process : The mineral is red
fine powder, mixed with five or six times its
carbonate, and the mixture is heated to whi
crucible placed within a well-covered eart
minutes or half an hour. The shrunken cohe
dilute hydrochloric acid, the whole evaporated
water added, and the silica separated by a fil
then mixed with ammonium carbonate in exces
the clear liquid is evaporated to dryness, an
platinum crucible, to expel the sal-ammoniac
wetted with oil of vitriol, gently evaporated o
and ignited : pure fused lithium sulphate then

This process will serve to give a good idea o
of the operation by which alkalis are extracted
and their quantities determined.

Lithium hydrate, LiHO, is much less solubl
hydrates of potassium and sodium ; the *carbon*
also sparingly soluble salts. The *chloride* cryst
cubes which are deliquescent. *Lithium sulpha*
salt ; it crystallises in lengthened prisms contai
water. It gives no double salt with aluminiu

CAESIUM AND RUBIDIUM.

Cs = 133. — Rb = 85·4.

THE two metals designated by these names were discovered by Bunsen and Kirchhoff by means of their spectrum apparatus mentioned on page 76: the former in 1860 and the latter in 1861. These metals, it appears, are widely diffused in nature, but always occur in very small quantities; they have been detected in many mineral waters, as well as in some minerals, namely, lithia-mica or lepidolite, and petalite; lately also in felspar; they have also been found in the alkaline ashes of beetroot. The salt-spring of Dürkheim, which contains 0·17 part of cæsium chloride in a million parts of water, was till lately regarded as the richest source of cæsium; but from recent experiments by Colonel Yorke,* it appears that the hot spring of Wheal Clifford, already mentioned as a source of lithium, contains 1·71 parts of cæsium chloride in a million, or 0·12 grains in a gallon. The best material for the preparation of rubidium is lepidolite, which has been found to contain as much as 0·2 per cent. of that metal. Both metals are closely analogous to potassium in their deportment, and cannot be distinguished from that metal or from one another, either by reagents or before the blow-pipe.

Rubidium and cæsium, like potassium, form double salts with tetrachloride of platinum, which are, however, much less soluble than the corresponding potassium salts: it is on this property that the separation of these metals from potassium is based. The mixture of platinochlorides is repeatedly extracted with boiling water, when a difficultly soluble residue, consisting chiefly of the platinochlorides of cæsium and rubidium, remains; and these two metals are finally separated by converting them into tartrates, rubidium tartrate requiring for solution eight times as much water as cæsium tartrate, and therefore crystallising out first from the mixed solution.

The hydroxides of these metals are powerful bases, which attract carbonic acid from the air, passing, first into normal carbonate, and then into acid carbonate. Cæsium carbonate is soluble in absolute alcohol; rubidium carbonate is nearly insoluble in that liquid: this property is made use of for the separation of these two metals. The chloride crystallises in cubes, and is somewhat more soluble in water than chloride of potassium.

Rubidium chloride, when in a state of fusion, is easily decomposed by the electric current; the metal produced rises to the surface and burns with a reddish light. If this experiment be performed in an atmosphere of hydrogen, to prevent oxidation, the separated metal is nevertheless lost, dissolving as it does in the fused chloride, which is transformed into a subchloride having the blue colour of

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* Journal of the Chemical Society, 1872, p. 273.

GROUP II.

SILVER.

Atomic weight, 108. Symbol, Ag (.

Silver is found in the metallic state, as sı
sulphide of antimony and sulphide of ars
iodide, and bromide. Among the principal
mentioned those of the Hartz mountains in G
in Norway, and, more particularly, of the An
South America.

The greater part of the silver of commerce
so poor as to render any process of *smelting*
even where fuel could be obtained, and this
procured. Recourse, therefore, is had to an
amalgamation—founded on the easy solubilit
other metals in metallic mercury.

The amalgamation process adopted in Ge
somewhat from that in use in America—is a
crushed to powder, mixed with a quantity
roasted at a low red heat in a suitable furnace
any sulphide of silver it may contain is co
The mixture of earthy matter, oxides of iro
salts, silver chloride, and metallic silver, is sif
barrels made to revolve on axes, with a quanti
of iron, and the whole is

&c., whereby it is brought into a pulverulent condition, known as "flouring," and is then liable to be washed away, together with the silver it has taken up. This inconvenience may be prevented, as suggested by Mr. Crookes, by amalgamating the mercury with 1 or 2 per cent. of sodium, which, by its superior affinity for sulphur and oxygen, prevents the mercury from becoming floured.

A considerable quantity of silver is obtained from argentiferous galena; in fact, almost every specimen of native lead sulphide is found to contain traces of this metal. When the proportion rises to a certain amount, it becomes worth extracting. The ore is reduced in the usual manner, the whole of the silver remaining with the lead; the latter is then re-melted in a large vessel, and allowed to cool slowly until solidification commences. The portion which first crystallises is nearly pure lead, the alloy with silver being *more fusible than lead itself:* by particular management this is drained away, and is found to contain nearly the whole of the silver [Pattinson's process]. This rich mass is next exposed to a red heat on the shallow hearth of a furnace, while a stream of air is allowed to impinge upon its surface; oxidation takes place with great rapidity, the fused oxide or litharge being constantly swept from the metal by the blast. When the greater part of the lead has been thus removed, the residue is transferred to a cupel or shallow dish made of bone-ashes, and again heated: the last portion of the lead is now oxidised, and the oxide sinks in a melted state into the porous vessel, while the silver, almost chemically pure, and exhibiting a brilliant surface, remains behind.

Pure silver may be easily obtained. The metal is dissolved in nitric acid: if it contains copper, the solution will have a blue tint; gold will remain undissolved as a black powder. The solution is mixed with hydrochloric acid or with common salt, and the white, insoluble, curdy precipitate of silver chloride is washed and dried. This is then mixed with about twice its weight of anhydrous sodium carbonate, and the mixture, placed in an earthen crucible, is gradually raised to a temperature approaching whiteness, during which the sodium carbonate and the silver chloride react upon each other; carbon dioxide and oxygen escape, while metallic silver and silver chloride result: the former melts into a button at the bottom of the crucible, and is easily detached. The following is perhaps the most simple method for the reduction of silver chloride. The silver-salt is covered with water, to which a few drops of sulphuric acid are added; a plate of zinc is then introduced. The silver chloride soon begins to decompose, and is, after a short time, entirely converted into metallic silver; the silver thus obtained is grey and spongy; it is ultimately purified by washing with slightly acidulated water.

Pure silver has a perfect white colour and a high degree of lustre: it is exceedingly malleable and ductile, and is probably the best conductor both of heat and electricity known. Its specific gravity is 10·5. In hardness it lies between gold and copper. It melts at a bright red heat. Silver is unalterable by air and moisture: it

when
matter, as glass, which it stains yellow or
of a silicate. It is little attacked by hydr
of vitriol converts it into sulphate, with
oxide ; nitric acid, even dilute and in the
The tarnishing of surfaces of silver expo
hydrogen sulphide, the metal having a stro

Silver Chlorides.—Two of these compo
ing respectively 1 and 2 atoms of silver to
second, however, is a very unstable compou

The *Monochloride* or *Argentic Ch*
invariably produced when a soluble silver s
are mixed. It falls as a white curdy preci
water and nitric acid ; one part of silver ch
parts of hydrochloric acid when concentrate
when diluted with double its weight of
melts, and on cooling becomes a greyish crys
like horn : it is found native in this conditio
silver of the mineralogist. Silver chloride i
both in the dry and in the wet state, ve
quickly if organic matter be present: it is
into water with metallic zinc or iron. It d
in ammonia and in a solution of potassium
the proportion of chlorine or hydrochloric
always estimated by precipitation with silve
is acidulated with nitric acid, and an excess
the chlorine is collected on a filter, or better
dried, and fused ; 100 parts correspond to 24
of hydrochloric acid.

Argentous Chloride, Ag_4Cl_2, is obtaine

Silver Fluoride, AgF, is produced by dissolving argentic oxide or carbonate in aqueous hydrofluoric acid, and separates on evaporation in transparent quadratic octohedrons, which contain $AgF.H_2O$, and give off their water when fused. Their solution gives, with hydrochloric acid, a precipitate of argentic chloride. When chlorine gas is passed over fused silver fluoride, silver chloride is formed and fluorine is set free (p. 203).

Silver Iodide, AgI, is a pale-yellow insoluble precipitate, produced by adding silver nitrate to potassium iódide; it is insoluble, or nearly so, in ammonia, and in this respect forms an exception to the silver-salts in general. Deville has obtained a crystalline silver iodide by the action of concentrated hydriodic acid upon metallic silver, which it dissolves with disengagement of hydrogen. Hydriodic acid converts silver chloride into iodide. The *bromide* of silver very closely resembles the chloride.

Silver Oxides.—There are three oxides of silver, only one of which can, however, be regarded as a well-defined compound, namely:

The *Monoxide,* or *Argentic Oxide,* Ag_2O.—This oxide is a powerful base, yielding salts isomorphous with those of the alkali-metals. It is obtained as a pale-brown precipitate on adding caustic potash to a solution of silver nitrate:

$$2AgNO_3 + KHO = Ag_2O + KNO_3 + HNO_3.$$

It is very soluble in ammonia, and is dissolved also to a small extent by pure water; the solution is alkaline. Recently precipitated silver chloride, boiled with a solution of caustic potash of specific gravity 1·25, is converted, according to Gregory, although with difficulty, into argentic oxide, which in this case is black and very dense. Argentic oxide neutralises acids completely, and forms, for the most part, colourless salts. It is decomposed by a red heat, with evolution of oxygen, spongy metallic silver being left: the sun's rays also effect its decomposition to a small extent.

Argentous Oxide, Ag_4O.*—When dry argentic citrate is heated to 100° in a stream of hydrogen gas, it loses oxygen and becomes dark-brown. The product, dissolved in water, gives a dark-coloured solution containing free citric acid and argentous citrate, which when mixed with potash yields a precipitate of argentous oxide. This oxide is a black powder, very easily decomposed, and soluble in ammonia. The solution of argentous citrate is rendered colourless by heat, being resolved into argentic citrate and metallic silver.

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* Assuming that this formula is correct, and that silver is a monad, then oxygen must be a tetrad; if, however, silver be regarded as a dyad or triad argentous oxide may be represented as $\begin{array}{ccc} Ag & \text{——} & Ag \\ | & & | \\ Ag & \text{—O—} & Ag \end{array}$, or as $\begin{array}{ccc} Ag & \text{——} & Ag \\ \| & & \| \\ Ag & \text{—O—} & Ag \end{array}$.

[illegible] of ammonia, wit
disengagement of nitrogen gas.

Oxysalts of Silver.—The *nitrate*, AgN
ing silver in nitric acid, and evaporating tl
until it is strong enough to crystallise on c
colourless, transparent, anhydrous tables, sc
of cold and in half that quantity of boiling
in alcohol. They fuse when heated, like
high temperature suffer decomposition: t
surgeon is silver nitrate which has been m
cylindrical mould. The salt blackens whe
particularly if organic matters of any ki
frequently employed to communicate a da
enters into the composition of the " indelibl
linen. The black stain has been thought t
may possibly be argentous oxide. Pure sil
pared from the metal alloyed with copper
in nitric acid, the solution evaporated to
nitrates cautiously heated to fusion. A sma
mass is removed from time to time for exan
in water, filtered, and ammonia added to it
copper-salt remains undecomposed, the liquid
that no longer happens, the nitrate may be su
in water, and filtered from the black oxide o

Silver Sulphate, Ag_2SO_4, may be prepared
of vitriol and metallic silver, or by precip
solution of silver nitrate with an alkaline su
88 parts of boiling water, and separates in
crystalline form on cooling, being but slig
temperature. It forms with ammonia a

Silver Carbonate is a white insoluble substance obtained by mixing solutions of silver nitrate and sodium carbonate. It is blackened and decomposed by boiling.

Silver Sulphide, Ag_2S, is a soft, grey, and somewhat malleable substance, found native in the crystallised state, and easily produced by melting together its constituents, or by precipitating a solution of silver with hydrogen sulphide. It is a strong sulphur-base, and combines with the sulphides of antimony and arsenic: examples of such compounds are found in the beautiful minerals, *dark* and *light-red silver ore.*

Ammonia Compound of Silver; *Berthollet's Fulminating Silver.*—This is a black, explosive compound formed by digesting precipitated argentic oxide in ammonia While moist, it explodes only when rubbed with a hard body, but when dry the touch of a feather is sufficient. The ammonia retains some of this substance in solution, and deposits it in small crystals by spontaneous evaporation. A similar compound exists containing oxide of gold.

Soluble silver salts are perfectly characterised by the white curdy precipitate of silver chloride, darkening by exposure to light, and insoluble in hot nitric acid, which is produced by the addition of any soluble *chloride.* Lead and mercury are the only metals which can be confounded with silver in this respect; but lead chloride is soluble to a great extent in boiling water, and is deposited in brilliant acicular crystals when the solution cools; and mercurous chloride is instantly blackened by ammonia, whereas silver chloride is dissolved thereby.

Solutions of silver are reduced to the metallic state by *iron, copper, mercury,* and other metals. They give with *hydrogen sulphide* a black precipitate of argentic sulphide insoluble in ammonium sulphide; with *caustic alkalis,* a brown precipitate of argentic oxide; and with *alkaline carbonates,* a white precipitate of argentic carbonate, both precipitates being easily soluble in ammonia. Ordinary *sodium phosphate* forms a yellow precipitate of argentic orthophosphate; *potassium chromate* or *bichromate,* a red brown precipitate of argentic chromate.

The economical uses of silver are many: it is admirably adapted for culinary and other similar purposes, not being attacked in the slightest degree by any of the substances used for food. It is necessary, however, in these cases, to diminish the softness of the metal by a small addition of copper. The standard silver of England contains 222 parts of silver and 18 parts of copper.

GOLD.

Atomic weight, 197. Symbol, Au (Aurum.)

GOLD, in small quantities, is a very widely diffused metal; traces of it are constantly found in the iron pyrites of the more ancient rocks. It is always met with in the metallic state, sometimes beautifully crystallised in the cubic form, associated with quartz, iron oxide, and other substances in regular mineral veins. The sands of various rivers have long furnished gold derived from this source, and separable by a simple process of washing; such is the *gold-dust* of commerce. When a veinstone is wrought for gold, it is stamped to powder, and shaken in a suitable apparatus with water and mercury; an amalgam is thus formed, which is afterwards separated from the mixture and decomposed by distillation. Formerly, the chief supply of gold was obtained from the mines of Brazil, Hungary, and the Ural mountains; but California and Australia now yield by far the largest quantity. The new gold-field of British Columbia is also very productive.

Native gold is almost always alloyed with silver. The purest specimens have been obtained from Schabrowski, near Katharinenburg, in the Ural. A specimen analysed by Gustav Rose was found to contain 98·96 per cent. of gold. The Californian gold averages from 87·5 to 88·5 per cent., and the Australian from 96 to 96·6 per cent. In some specimens of native gold, as in that from Linarowski in the Altai mountains, the percentage of gold is as low as 60 per cent. the remainder being silver.

Pure gold is obtained from its alloys by solution in nitromuriatic acid, and precipitated with a ferrous salt, which reduces the gold, and is itself converted into a ferric salt, thus:

$$6FeSO_4 + 2AuCl_3 = 2Fe_2(SO_4)_3 + Fe_2Cl_6 + Au_2.$$

The gold falls as a brown powder, which acquires the metallic lustre by friction.

Gold is a soft metal, having a beautiful yellow colour. It surpasses all other metals in malleability, the thinnest gold leaf not exceeding, it is said, $\frac{1}{200,000}$ of an inch in thickness, while the gilding on the silver wire used in the manufacture of *gold-lace* is still thinner. It may also be drawn into very fine wire. Gold has a density of 19·5: it melts at a temperature a little above the fusing point of silver. Neither air nor water affects it in the least at any temperature; the ordinary acids fail to attack it singly. A mixture of nitric and hydrochloric acid dissolves gold, however, with ease, the active agent being the liberated chlorine.

Gold forms two series of compounds: the *aurous compounds*, in which it is univalent, as $AuCl$, Au_2O, &c., and the *auric compounds*, in which it is trivalent, as $AuCl_3$, Au_2O_3, &c.

Chlorides.—The *monochloride* or *Aurous chloride*, AuCl, is produced when the trichloride is evaporated to dryness, and exposed to a heat of 227° until chlorine ceases to be exhaled. It forms a yellowish-white mass, insoluble in water. In contact with that liquid it is decomposed slowly in the cold, and rapidly by the aid of heat, into metallic gold and trichloride.

The *trichloride* or *Auric chloride*, $AuCl_3$, is the most important compound of gold: it is always produced when gold is dissolved into nitro-muriatic acid. The deep yellow solution thus obtained yields, by evaporation, yellow crystals of the double chloride of gold and hydrogen; when this is cautiously heated, hydrochloric acid is expelled, and the residue, on cooling, solidifies to a red crystalline mass of auric chloride, very deliquescent, and soluble in water, alcohol, and ether. Auric chloride combines with a number of metallic chlorides, forming a series of double salts, called chloroaurates, of which the general formula in the anhydrous state is $MCl.AuCl_3$, M representing an atom of a monad metal. These compounds are mostly yellow when in crystals, and red when deprived of water. The *ammonium salt*, $NH_4Cl.AuCl_3.H_2O$, crystallises in transparent needles; the sodium salt, $NaCl.AuCl_3.2H_2O$, in long four-sided prisms. Auric chloride likewise forms crystalline double salts with the hydrochlorides of many organic bases.

A mixture of auric chloride with excess of acid potassium or sodium carbonate is used for gilding small ornamental articles of copper: these are cleaned by dilute nitric acid, and then boiled in the mixture for some time, by which means they acquire a thin but perfect coating of reduced gold.

Oxides.—The *monoxide*, or *Aurous oxide*, is produced when caustic potash in solution is poured upon the monochloride. It is a green powder, partly soluble in the alkaline liquid; the solution rapidly decomposes into metallic gold, which subsides, and auric oxide, which remains dissolved.

Trioxide or *Auric oxide*, Au_2O_3.—When magnesia is added to auric chloride, and the sparingly soluble aurate of magnesium well washed and digested with nitric acid, auric oxide is left as an insoluble reddish-yellow powder, which when dry becomes chestnut-brown. It is easily reduced by heat, and by mere exposure to light; it is insoluble in oxygen-acids, with the exception of strong nitric acid, insoluble in hydrofluoric acid, easily dissolved by hydrochloric and hydrobromic acids. Alkalis dissolve it freely; indeed, the acid properties of this substance are very strongly marked; it partially decomposes a solution of potassium chloride when boiled with that liquid, potassium hydroxide being produced. When digested with ammonia, it yields fulminating gold, consisting, according to Berzelius, of $Au_2O_3.4NH_3.H_2O$.

The compounds of auric oxide with alkalis are called aurates. The *potassium salt*, $K_2O.Au_2O_3.6H_2O$ or $KAuO_2.3H_2O$, is a crystalline salt, the solution of which is sometimes used as a bath for electro-gilding. A compound of aurate and acid sulphite of potassium, or *potassium aurosulphite*, $2(KAuO_2.4KHSO_3).H_2O$, is deposited in yellow needles when potassium sulphite is added, drop by drop, to an alkaline solution of potassium aurate.

Gold shows but little tendency to form oxygen-salts. Auric oxide dissolves in strong nitric acid, but the solution is decomposed by evaporation or dilution. A *sodio-aurous thiosulphate*, $Na_3Au(S_2O_3)_2.2H_2O$, is prepared by mixing the concentrated solutions of auric chloride and sodium thiosulphate, and precipitating with alcohol. It is very soluble in water, and crystallises in colourless needles. Its solution is used for fixing daguerreotype pictures. With barium chloride, it yields a gelatinous precipitate of *bario-aurous thiosulphate*, $Ba_3Au_2(S_2O_3)_4$.

Sulphides.—*Aurous sulphide*, Au_2S, is formed as a dark-brown, almost black precipitate when hydrogen sulphide is passed into a boiling solution of auric chloride. It forms sulphur-salts with the monosulphides of potassium and sodium. *Auric sulphide*, Au_2S_3, is precipitated in yellow flocks when hydrogen sulphide is passed into a cold dilute solution of auric chloride. Both these sulphides dissolve in ammonium sulphide.

The presence of gold in solution may be detected by the brown precipitate with *ferrous sulphate*, fusible before the blowpipe to a bead of metallic gold; also by the brownish purple precipitate, called "Purple of Cassius," formed when *stannous chloride* is added to dilute gold solutions. The composition of this precipitate is not exactly known, but after ignition it doubtless consists of a mixture of stannic oxide and metallic gold.* It is used in enamel painting.

Oxalic acid slowly reduces gold to the metallic state: to ensure complete precipitation, the gold-solution must be digested with it for 24 hours. For the quantitative analysis of a solution containing gold and other metals, oxalic acid is in most cases a more convenient precipitant than ferrous sulphate; inasmuch as, if the quantities of the other metals are also to be determined, the presence of a large quantity of iron salt may complicate the analysis considerably.

Gold intended for coin, and most other purposes, is always alloyed with a certain proportion of silver or copper, to increase its hardness and durability: the first-named metal confers a pale greenish colour. English standard gold contains $\frac{1}{12}$ of alloy, now always copper. Gold when alloyed with copper may be estimated by fusion in a cupel with lead, in the same way as silver (p. 367). If the alloy be free from silver, the weight of the globule of gold left in the cupel will, after repeated fusions, accurately represent the quantity of gold which is present in the alloy. But if the alloy contains silver, that metal remains with the gold after cupellation. In this case the original alloy, consisting of gold, silver, and copper, is fused in the muffle, together with lead and silver; the alloy of gold and silver remaining after cupellation is then boiled with nitric acid, which dissolves the silver, the gold being left behind. By treatment of the alloy of gold and silver with nitric acid, an accurate separation is obtained only when the two metals are present in certain proportions. If the alloy contains but little silver, that metal is protected from the action of the nitric acid by the gold; again, if it contains too much silver, the gold is left as a powder when the silver is dissolved out. Experience has shown that the most favourable proportions are $\frac{1}{4}$ gold to $\frac{3}{4}$ silver; the gold is then left pure, retaining the original shape of the alloy, and can be easily dried and weighed. The quantity of silver which is added to the alloy must therefore vary with the amount of gold which it contains.

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* Graham's Elements of Chemistry, 2nd edit. vol. ii. p. 353.

Gold-leaf is made by rolling out plates of pure gold as thin as possible, and then beating them between folds of membrane with a heavy hammer, until the requisite degree of tenuity has been reached. The leaf is made to adhere to wood, &c., by size or varnish.

Gilding on copper has very generally been performed by dipping the articles into a solution of mercury nitrate, and then shaking them with a small lump of a soft amalgam of gold with that metal, which thus becomes spread over their surfaces: the articles are subsequently heated to expel the mercury, and then burnished. Gilding on steel is done either by applying a solution of auric chloride in ether, or by roughening the surface of the metal, heating it, and applying gold-leaf with the burnisher. Gilding by electrolysis—an elegant and simple method, now rapidly superseding many of the others—has already been noticed (p. 299). The solution usually employed is obtained by dissolving oxide or cyanide of gold in a solution of potassium cyanide.

CLASS II.—DYAD METALS.

GROUP I.—METALS OF THE ALKALINE EARTHS.

BARIUM.*

Atomic weight, 137. Symbol, Ba.

THIS metal occurs abundantly as sulphate and carbonate, forming the *veinstone* in many lead mines. Davy obtained it in the metallic state by means similar to those described in the case of lithium. Bunsen subjects barium chloride mixed to a paste with water and a little hydrochloric acid, at a temperature of 100°, to the action of the electric current, using an amalgamated platinum wire as the negative pole. In this manner the metal is obtained as a solid, highly crystalline amalgam, which, when heated in a stream of hydrogen, yields barium in the form of a tumefied mass, tarnished on the surface, but often exhibiting a silver-white lustre in the cavities. Barium may also be obtained, though impure, by passing vapour of potassium over the red-hot chloride or oxide of barium. It is malleable, melts below a red heat, decomposes water, and gradually oxidises in the air.

Barium Chloride, $BaCl_2.2H_2O$.—This valuable salt is prepared by dissolving the native carbonate in hydrochloric acid, filtering the solution, and evaporating until a pellicle begins to form at the surface : the solution on cooling deposits crystals. When native carbonate cannot be procured, the native sulphate may be employed in the following manner :—The sulphate is reduced to fine powder, and intimately mixed with one-third of its weight of powdered coal; the mixture is pressed into an earthen crucible to which a cover is fitted, and exposed for an hour or more to a high red heat, by which the sulphate is converted into sulphide at the expense of the combustible matter of the coal; the black mass thus obtained is powdered and boiled in water, by which the sulphide is dissolved; and the solution, filtered hot, is mixed with a slight excess of hydrochloric acid. Barium chloride and hydrogen sulphide are then produced, the latter escaping with effervescence. Lastly, the solution is filtered to separate any little insoluble matter, and evaporated to the crystallising point.

The crystals of barium chloride are flat four-sided tables, colourless and transparent. They contain two molecules of water, easily driven off by heat. 100 parts of water dissolve 43·5 parts at 15·5°, and 78 parts at 104·5°, which is the boiling-point of the saturated solution.

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* From βαρύς, heavy, in allusion to the great specific gravity of the native carbonate and sulphate.

Barium Oxides.—The *Monoxide* or *Baryta*, BaO, is best prepared by decomposing the crystallised nitrate by heat in a capacious porcelain crucible until red vapours are no longer disengaged: the nitric acid is then resolved into nitrous acid and oxygen, and the baryta remains behind in the form of a greyish spongy mass, fusible at a high degree of heat. When moistened with water it combines into a hydrate, with great elevation of temperature. The *Hydroxide* or *Hydrate*, $BaH_2O_2 = BaO.H_2O$, is prepared on the large scale by decomposing a hot concentrated solution of barium chloride with a solution of caustic soda; on cooling, crystals of barium hydrate are deposited, which may be purified by re-crystallisation. In the laboratory barium hydrate is often prepared by boiling a strong solution of the sulphide with small successive portions of black oxide of copper until a drop of the liquid ceases to form a black precipitate with lead salts: the filtered liquid on cooling yields crystals of the hydrate. The crystals of barium hydrate contain $BaH_2O_2.8\,aq.$;[*] they fuse easily, and lose their water of crystallisation when strongly heated, leaving the hydrate, BaH_2O_2, in the form of a white, soft powder, having a great attraction for carbonic acid, and soluble in 20 parts of cold and 2 parts of boiling water. The solution is a valuable reagent: it is highly alkaline to test-paper, and instantly rendered turbid by the smallest trace of carbonic acid.

The *Dioxide*, BaO_2, may be formed, as already mentioned, by exposing baryta, heated to full redness in a porcelain tube, to a current of pure oxygen gas. It is grey, and forms with water a white hydrate, which is not decomposed by that liquid in the cold, but dissolves in small quantity. Barium hydrate, when heated to redness in a current of dry atmospheric air, loses its water, and is converted, by absorption of oxygen, into barium dioxide, from which the second atom of oxygen may be expelled at a higher temperature. Boussingault has proposed to utilise these reactions for the preparation of oxygen upon a large scale. The dioxide may also be made by heating pure baryta to redness in a platinum crucible, and then gradually adding an equal weight of potassium chlorate, whereby barium dioxide and potassium chloride are produced. The latter may be extracted by cold water, and the dioxide left in the state of hydrate. It is used for the preparation of hydrogen dioxide (p. 145). When dissolved in dilute acid, it is decomposed by potassium bichromate, and by the oxide, chloride, sulphate, and carbonate of silver.

Oxysalts of Barium.—The *Nitrate*, $Ba(NO_3)_2$, is prepared by methods exactly similar to those adopted for preparing the chloride, nitric acid being substituted for hydrochloric. It crystallises in transparent colourless octohedrons, which are anhydrous. They require for solution 8 parts of cold and 3 parts of boiling water. This salt is much less soluble in dilute nitric acid than in pure water: errors sometimes arise from such a precipitate of crystalline barium nitrate being mistaken for sulphate. It disappears on heating, or by large affusion of water.

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[*] The symbol, aq. (abbreviation of *aqua*) is often used to denote water of crystallisation.

The *Sulphate*, $BaSO_4$, is found native as *heavy spar* or *barytes*, often beautifully crystallised: its specific gravity is as high as 4·4 to 4·8. This compound is always produced when sulphuric acid or a soluble sulphate is mixed with a solution of a barium salt. It is not sensibly soluble in water or in dilute acids: even in nitric acid it is almost insoluble: hot oil of vitriol dissolves a little, but the greater part separates again on cooling Barium sulphate is now produced artificially on a large scale, and is used as a substitute for white-lead in the manufacture of oil-paints. The sulphate to be used for this purpose is precipitated from very dilute solutions: it is known in commerce as *blanc fixe*. Powdered native barium sulphate, being rather crystalline, has not sufficient body. For the production of sulphate, the chloride of barium is first prepared, which is dissolved in a large quantity of water, and then precipitated by dilute sulphuric acid.

The *Carbonate*, $BaCO_3$, is found native as *witherite*, and may be formed artificially by precipitating the chloride or nitrate with an alkaline carbonate, or carbonate of ammonia. It is a heavy, white powder, very sparingly soluble in water, and chiefly useful in the preparation of other barium salts.

Barium Sulphides.—The *Monosulphide*, BaS, is obtained in the manner already described (p. 376); the higher sulphides may be formed by boiling it with sulphur. Barium monosulphide crystallises from a hot solution in thin, nearly colourless plates, which contain water, and are not very soluble: they are rapidly altered by the air. A strong solution of this sulphide may be employed, as already described, in the preparation of barium hydrate.

Solutions of barium hydrate, nitrate, and chloride, are constantly kept in the laboratory as chemical tests, the first being employed to effect the separation of carbonic acid from certain gaseous mixtures, and the two latter to precipitate sulphuric acid from solution.

Soluble barium salts are poisonous, which is not the case with those of strontium. For their reactions, see page 387.

STRONTIUM.

Atomic weight, 87·6. Symbol, Sr.

THE metal strontium may be obtained from its oxide by means similar to those described in the case of barium: it is usually described as a white metal, heavy, oxidisable in the air, and capable of decomposing water at common temperatures. Matthiessen states, however, that it has a dark-yellow colour, and specific gravity 2·54. He prepares it by filling a small crucible having a porous cell with anhydrous strontium chloride mixed with some ammonium chloride, so that the level of the fused chloride in the cell is much higher than in the crucible. The negative pole placed in the cell consists of a very fine iron wire. The positive pole is an iron cylinder placed in the crucible round the cell. The heat is regulated so that a crust forms in the cell, and the metal collects under this crust.

Strontium Monoxide, or *Strontia*, SrO, is best prepared by decomposing the nitrate with aid of heat: it resembles baryta in almost every particular, forming, like that substance, a white hydrate, soluble in water. A hot saturated solution deposits crystals on cooling, which contain $SrH_2O_2.8$ aq.: heated to dull redness they lose the whole of their water, anhydrous strontia being left. The hydrate has a great attraction for carbonic acid. The *Dioxide*, SrO_2, is prepared in the same manner as barium dioxide: it may be substituted for the latter in making hydrogen dioxide.

The native carbonate and sulphate of strontium serve for the preparation of the various salts by means exactly similar to those already described in the case of barium salts: they have a very feeble degree of solubility in water.

Strontium Chloride, $SrCl_2$, crystallises in colourless needles or prisms, which are slightly deliquescent, and soluble in 2 parts of cold and a still smaller quantity of boiling water: they are also soluble in alcohol, and the solution, when kindled, burns with a crimson flame. The crystals contain 6 molecules of water, which they lose by heat: at a higher temperature the chloride fuses.

Strontium Nitrate, $Sr(NO_3)_2$, crystallises in anhydrous octohedrons, which require for solution 5 parts of cold and about half their weight of boiling water. It is principally of value to the pyrotechnist, who employs it in the composition of the well-known "red fire."*

The spectral phenomena exhibited by strontium compounds are mentioned on page 77.

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* RED FIRE:	Grains.	GREEN FIRE:	Grains.
Dry strontium nitrate.	800	Dry barium nitrate, .	450
Sulphur, . .	225	Sulphur, . . .	150
Potassium chlorate,	200	Potassium chlorate, .	100
Lampblack, . .	50	Lampblack, . . .	25

The strontium or barium-salt, the sulphur, and the lampblack, must be finely powdered and intimately mixed, after which the potassium chlorate

CALCIUM.

Atomic weight, 40. Symbol, Ca.

Calcium is one of the most abundant and widely diffused of the metals, though it is never found in the free state. As carbonate, it occurs in a great variety of forms, constituting, as limestone, entire mountain ranges. Calcium was obtained in an impure state by Davy, by means similar to those adopted for the preparation of barium. Matthiessen prepares the pure metal by fusing a mixture of two molecules of calcium chloride and one of strontium chloride with some chloride of ammonium in a small porcelain crucible, in which an iron cylinder is placed as positive pole, and a pointed iron wire or a little rod of carbon connected with the zinc of the battery is made to touch the surface of the liquid. The reduced metal fuses and drops off from the point of the iron wire, and the bead is removed from the liquid by a small iron spatula. Liès-Bodart and Gobin prepare calcium by igniting the iodide with an equivalent quantity of sodium in an iron crucible having its lid screwed down.

Calcium is a light yellow metal of sp. gr. 1·5778. It is about as hard as gold, very ductile, and may be cut, filed, or hammered out into plates as thin as the finest paper. It tarnishes slowly in dry, more quickly in damp air, decomposes water quickly, and is still more rapidly acted upon by dilute acids. Heated on platinum foil over a spirit-lamp, it burns with a bright flash ; with a brilliant light also when heated in oxygen or chlorine gas, or in vapour of bromine, iodine, or sulphur.

Calcium Chloride, $CaCl_2$, is usually prepared by dissolving marble in hydrochloric acid ; it is also a bye-product in several chemical manufactures. The salt separates from a strong solution in colourless, prismatic, and exceedingly deliquescent crystals, which contain 6 molecules of water. By heat this water is expelled, and by a temperature of strong ignition the salt is fused. The crystals reduced to powder are employed in the production of artificial cold by being mixed with snow or powdered ice; and the chloride, strongly dried, or in the fused state, is of great use in desiccating gases, for which purpose the latter are slowly transmitted through tubes filled with fragments of the salt. Calcium chloride is also freely soluble in alcohol, which, when anhydrous, forms with it a definite crystallisable compound.

Calcium Fluoride, Fluor-Spar, CaF_2.—This substance is important as the most abundant natural source of hydrofluoric acid and the other fluorides. It occurs beautifully crystallised, of various colours,

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should be added in rather coarse powder, and mixed, without much rubbing, with the other ingredients. The red fire composition has been known to ignite *spontaneously*.

in lead-veins, the crystals having commonly the cubic, but sometimes the octohedral form, parallel to the faces of which latter figure they always cleave. Some varieties, when heated, emit a greenish, and some a purple phosphorescent light. The fluoride is quite insoluble in water, and is decomposed by oil of vitriol in the manner already mentioned (p. 203).

Calcium Oxides.—The *Monoxide* or *Lime*, CaO, may be obtained in a state of considerable purity by heating to full redness for some time fragments of the black bituminous marble of Derbyshire or Kilkenny. If required absolutely pure, it must be made by igniting to whiteness, in a platinum crucible, an artificial calcium carbonate, prepared by precipitating the nitrate with ammonia carbonate. Lime in an impure state is prepared for building and agricultural purposes by calcining, in a kiln of suitable construction, the ordinary limestones which abound in many districts; a red heat, continued for some hours, is sufficient to disengage the whole of the carbonic acid. In the best-contrived lime-kilns the process is carried on continuously, broken limestone and fuel being constantly thrown in at the top, and the burned lime raked out at intervals from beneath. Sometimes, when the limestone contains silica, and the heat has been very high, the lime refuses to slake, and is said to be *overburned;* in this case a portion of silicate has been formed.

Pure lime is white, and often of considerable hardness: it is quite infusible, and phosphoresces, or emits a pale light at a high temperature. When moistened with water, it slakes with great violence, evolving heat, and crumbling to a soft, white, bulky powder, which is a hydrate containing a single molecule of water: the latter can be again expelled by a red heat. This hydrate or hydroxide, CaH_2O_2 or $CaO.H_2O$, is soluble in water, but far less so than either the hydrate of barium or of strontium, and, what is very remarkable, the *colder* the water, the larger is the quantity of the compound that is taken up. A pint of water at 15·5° dissolves about 11 grains, while at 100° only 7 grains are retained in solution. The hydrate has been obtained in thin delicate crystals by slow evaporation under the air-pump. Lime-water is always prepared for chemical and pharmaceutical purposes by agitating cold water with excess of calcium hydrate in a closely-stopped vessel, and then, after subsidence, pouring off the clear liquid, and adding a fresh quantity of water, for another operation: there is not the least occasion for filtering the solution. Lime-water has a strong alkaline reaction, a nauseous taste, and when exposed to the air becomes almost instantly covered with a pellicle of carbonate, by absorption of carbonic acid. It is used, like baryta-water, as a test for carbonic acid, and also in medicine. Lime-water prepared from some varieties of limestone may contain potash.

The hardening of mortars and cements is in a great measure due to the gradual absorption of carbonic acid; but even after a very great length of time, this conversion into carbonate is not complete. Mortar is known, under favourable circumstances, to acquire extreme hardness with age. Lime cements which resist the action of water contain iron oxides, silica, and alumina: they require to be carefully prepared, and the stone not over-heated. When they are ground to powder and mixed with water, solidification speedily ensues, from causes not yet thoroughly understood, and the cement, once in this condition, is unaffected by wet. Parker's or Roman cement is made in this manner from the nodular masses of calcareo-argillaceous ironstone found in the London clay.

Lime is of great importance in agriculture: it is found more or less in every fertile soil, and is often very advantageously added by the cultivator. The decay of vegetable fibre in the soil is thereby promoted, and other important objects, as the destruction of certain hurtful compounds of iron in marsh and peat land, are often attained. The addition of lime probably serves likewise to liberate potassium from the insoluble silicate of that base contained in the soil.

Calcium Dioxide, CaO_2, is said to resemble barium dioxide, and to be obtainable by treating lime with hydrogen dioxide.

Calcium Sulphate, $CaSO_4$.—Crystalline native calcium sulphate, containing two molecules of water, is found in considerable abundance in some localities as *gypsum:* it is often associated with rock-salt. When regularly crystallised, it is termed *selenite*. Anhydrous calcium sulphate is also occasionally met with. The salt is formed by precipitation, when a moderately concentrated solution of calcium chloride is mixed with sulphuric acid. Calcium sulphate is soluble in about 500 parts of cold water, and its solubility is a little increased by heat. It is more soluble in water containing ammonium chloride or potassium nitrate. The solution is precipitated by alcohol. Gypsum, or native hydrated calcium sulphate, is largely employed for the purpose of making casts of statues and medals, also for moulds in the porcelain and earthenware manufactures, and for other applications. It is exposed to heat in an oven where the temperature does not exceed 127°, by which the water of crystallisation is expelled, and it is afterwards reduced to a fine powder. When mixed with water, it solidifies after a short time, from the re-formation of the same hydrate; but this effect does not happen if the gypsum has been over-heated. It is often called Plaster of Paris. Artificial coloured marbles, or *scagliola*, are frequently prepared by inserting pieces of natural stone in a soft stucco containing this substance, and polishing the surface when the cement has become hard. Calcium sulphate is one of the most common impurities of spring water.

The peculiar property water acquires by the presence of calcium salts is termed *hardness*. It manifests itself by the effect such waters have upon the palate, and particularly by its peculiar behaviour with soap. Hard water yields a lather with soap only after the whole of the calcium salts have been thrown down from the water in the form of an insoluble lime-soap. Upon this principle Clark's *soap-test* for the hardness of water is based. The hardness produced by calcium sulphate is called *permanent hardness*, since it cannot be remedied.

Calcium Carbonate, *Chalk; Limestone; Marble;* $CaCO_3$.—Calcium carbonate, often more or less contaminated with iron oxide, clay, and organic matter, forms rocky beds, of immense extent and thickness, in almost every part of the world. These present the greatest diversities of texture and appearance, arising, in a great measure, from changes to which they have been subjected since their deposition. The most ancient and highly crystalline limestones are destitute of visible organic remains, while those of more recent origin are often entirely made up of the shelly exuviæ of once-living beings. Sometimes these latter are of such a nature as to show that the animals inhabited fresh water; marine species and corals are, however, most abundant. Cavities in limestone and other rocks are very often lined with magnificent crystals of calcium carbonate or calcareous spar, which have evidently been slowly deposited from a watery solution. Calcium carbonate is always precipitated when an alkaline carbonate is mixed with a solution of that base.

Although this substance is not sensibly soluble in pure water, it is freely taken up when carbonic acid happens at the same time to be present. If a little lime-water be poured into a vessel of that gas, the turbidity first produced disappears on agitation, and a transparent solution of calcium carbonate in excess of carbonic acid is obtained. This solution is decomposed completely by boiling, the carbonic acid being expelled, and the carbonate precipitated. Since all natural waters contain dissolved carbonic acid, it is to be expected that calcium in this state should be of very common occurrence; and such is really found to be the fact, river, and more especially spring water, almost invariably containing calcium carbonate thus dissolved. In limestone districts, this is often the case to a great extent. The *hardness* of water, which is owing to the presence of calcium carbonate, is called *temporary*, since it is diminished to a very considerable extent by boiling, and may be nearly removed by mixing the hard water with lime-water, when both the dissolved carbonate and the dissolved lime, which thus becomes carbonated, are precipitated. Upon this principle Dr. Clark's process of softening water is based. This process is of considerable importance, since a supply of hard water to towns is in many respects a source of great inconvenience. As already mentioned, the use of such water, for the purposes of washing, is attended with a great loss of soap. Boilers, in which such water is heated, speedily become lined wtih a thick stony incrustation.*

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* Many proposals have been made to prevent the formation of boiler deposits. The most efficient appears to be the method of Dr. Ritterband, which consists in throwing into the boiler a small quantity of sal-ammoniac, whereby carbonate of ammonia is formed, which is volatilised with the steam, calcium chloride remaining in solution. It need scarcely be mentioned that this plan is inapplicable in the case of permanently hard waters.

calc-spar when de
water containing carbonic acid at the o
90°, and on ebullition however, it is chie
of arragonite ; at lower temperatures th
decreases, whilst that of calc-spar increases,
of the former variety being between 30° a

Calc-spar occurs very abundantly in
obtuse rhombohedron, whose angles measu
density varies from 2·5 to 2·8. The rarer
found in crystals whose primary form is
figure having no geometrical relation to th
heavier and harder.

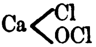
Calcium Phosphates.—A number of
phosphoric acid are known. Two *tribasic ph*
$Ca_3(PO_4)_2$ and $CaH(PO_4)$, are produced v
sodium salts are added in solution to calci
slightly crystalline, and the second gelati
phosphate is digested with ammonia, or di
precipitated by that alkali, it is converted
earth of bones consists principally of wha
bination of these two salts. Another ortho
is formed by dissolving either of the pr
hydrochloric, or nitric acid, and evaporating
on cooling in small platy crystals. It is th
phosphorus when heated with charcoal, in
manufacture before described. *Pyrophosph*
of calcium also exist. These phosphates,
water, dissolve readily in dilute acids, ev
mineral *apatite* is chiefly calcium phosphate.

unaltered hydrate being left behind: the solution is highly alkaline, and bleaches feebly. When calcium hydrate is suspended in cold water, and chlorine gas transmitted through the mixture, the lime is gradually dissolved, and the same peculiar bleaching compound produced: the alkalis also, either caustic or carbonated, may by similar means be made to absorb a large quantity of chlorine, and give rise to corresponding compounds; such are the "disinfecting solutions" of Labarraque.

The composition of bleaching powder is represented by the formula $CaOCl_2$, and it was formerly supposed to be a direct compound of lime with chlorine. This view, however, is not consistent with its reactions, for when distilled with dilute nitric acid, it readily yields a distillate of aqueous hypochlorous acid, and when treated with water it is resolved into chloride and hypochlorite of calcium, the latter of which may be separated in crystals by exposing the filtered solution to a freezing mixture, or by evaporating it in a vacuum over oil of vitriol, and leaving the dense frozen mass to thaw upon a filter. A solution of calcium chloride mixed with hypochlorite then passes through, and feathery crystals remain on the filter, very unstable, but consisting, when recently prepared, of hydrated calcium hypochlorite, $Ca(OCl)_2.4H_2O$.* These results seem at first sight to show that the bleaching powder is a mixture of chloride and hypochlorite of calcium, formed according to the equation,

$$2CaO + Cl_4 = CaCl_2 + CaCl_2O_2;$$

but if this were its true constitution, the powder, when digested with alcohol, ought to yield a solution of calcium chloride containing half the chlorine of the original compound, which is not the case. Its constitution is therefore better represented by the formula



$Ca\genfrac{}{}{0pt}{}{<Cl}{<OCl}$, suggested by Dr. Odling, this molecule being decomposed by water into chloride and hypochlorite in the manner just explained, and yielding, with dilute nitric or sulphuric acid, a distillate containing hydrochloric and hypochlorous acids:

$$CaCl(OCl) + 2HNO_3 = Ca(NO_3)_2 + HCl + HClO.$$

When the temperature of the calcium hydrate has risen during the absorption of the chlorine, or when the compound has been subsequently exposed to heat, its bleaching properties are impaired or altogether destroyed: it then contains chlorate and chloride of calcium; oxygen, in variable quantity, is usually set free. The same change seems to ensue by long keeping, even at the common temperature of the air. In an open vessel the compound is speedily decomposed by the carbonic acid of the air. Commercial bleaching powder thus constantly varies in value with its age, and with the care originally bestowed upon its preparation: the best may contain about 30 per cent. of available chlorine, easily liberated by an acid, which is however, far short of the theoretical quantity.

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* Kingzett, Chem. Soc. Jour. 1875, p. 404.

The general method in which this substance is employed for bleaching is the following :—The goods are first immersed in a dilute solution of chloride of lime, and then transferred to a vat containing dilute sulphuric acid. Decomposition ensues ; the calcium both of the hypochlorite and of the chloride is converted into sulphate, while the free hypochlorous and hydrochloric acids yield water and free chlorine :—

$$CaCl_2O_2 + CaCl_2 + 2H_2SO_4 = 2CaSO_4 + 2HClO + 2HCl,$$

and

$$HClO + HCl = H_2O + Cl_2.$$

The chlorine thus disengaged in contact with the cloth causes destruction of the colouring matter. The process is repeated several times, since it is unsafe to use strong solutions.

On the same principle, white patterns are imprinted upon coloured cloth, the figures being stamped with tartaric acid thickened with gum-water, and then the stuff immersed in the chlorine bath, when the parts to which no acid has been applied remain unaltered, while the printed portions are bleached.

For purifying an offensive or infectious atmosphere, *as an aid to proper ventilation*, the bleaching powder is very convenient. The solution is exposed in shallow vessels, or cloths steeped in it are suspended in the apartment, when the carbonic acid of the air slowly decomposes it in the manner above described. Addition of a strong acid causes rapid disengagement of chlorine.

The value of any sample of bleaching powder may be easily determined by the following method, in which the feebly combined chlorine is estimated by its effect in oxidising a ferrous salt to ferric salt, 2 molecules of ferrous oxide, FeO, requiring for this purpose 2 atoms of chlorine: the latter acts by decomposing water and liberating a corresponding quantity of oxygen. 78 (more correctly 78·16) grains of green ferrous sulphate are dissolved in about two ounces of water, and acidulated with a few drops of sulphuric or hydrochloric acid: this quantity will require for oxidation 10 grains of chlorine. Fifty grains of the chloride of lime to be examined are next rubbed up with a little tepid water, and the whole transferred to a burette (p. 352), which is then filled up to 0 with water, after which the contents are well mixed by agitation. The liquid is next gradually poured into the solution of iron, with constant stirring, until all the iron is brought to the state of ferric salt, which may be known by a drop ceasing to give a deep-blue precipitate with potassium ferrocyanide. The number of grain-measures of the chloride solution employed may then be read off : since these must contain 10 grains of serviceable chlorine, the quantity of the latter in the 50 grains may be easily reckoned. Thus, suppose 72 such measures have been taken; then

Measures.		Grs. Chlorine.		Measures.		Grs. Chlorine.
72	:	10	=	100	:	13·89

The bleaching powder contains therefore 27·78 per cent.*

Calcium Sulphides.—The monosulphide, CaS, is obtained by reducing the sulphate at a high temperature with charcoal or hydrogen: it is nearly colourless, and but little soluble in water. By boiling together calcium hydrate, water, and flowers of sulphur, a red solution is obtained, which, on cooling, deposits crystals of the bisulphide, CaS_2, containing water. When the sulphur is in excess, and the boiling long continued, a pentasulphide is generated: thiosulphuric acid is formed as usual during these reactions:

$$3CaO + S_6 = 2CaS_2 + CaS_2O_3.$$

When the yellow solution obtained by boiling lime with excess of sulphur is poured into an excess of hydrochloric acid, sulphur is precipitated together with a yellow oily liquid, which is hydrogen persulphide (p. 207); but if the acid be poured into the solution of calcium sulphide, gaseous hydrogen sulphide is given off, and the whole precipitate formed consists wholly of finely divided sulphur, the *sulphur precipitatum* of the Pharmacopœia. If dilute sulphuric acid is used, the precipitate also contains gypsum.

Calcium Phosphide.—When vapour of phosphorus is passed over fragments of lime heated to redness in a porcelain crucible, a chocolate-brown compound, the so-called *phosphuret of lime*, is produced. This substance is probably a mixture of calcium phosphide and phosphate. When thrown into water it yields spontaneously inflammable hydrogen phosphide. According to Paul Thénard, the calcium phosphide in this compound has the composition P_2Ca_2. In contact with water it yields liquid hydrogen phosphide, P_2H_4 (p. 239).

$$P_2Ca_2 + 2H_2O = 2CaO + P_2H_4:$$

and the greater portion of this liquid phosphide is immediately decomposed into solid and gaseous hydrogen phosphide: $5P_2H_4 = P_4H_2 + 6PH_3$.

Reactions of the Alkaline Earth-metals in solution.—Barium, strontium, and calcium are thus distinguished from all other substances, and from each other.

Caustic Potash, when free from carbonate, and caustic *ammonia*, occasion no precipitates in *dilute* solutions of the alkaline earths, especially of the first two, the hydrates being soluble in water.

Alkaline carbonates, and *carbonate of ammonia*, give white precipitates, insoluble in excess of the precipitant, with all three.

Sulphuric acid, or a *sulphate*, added to very dilute solutions of the salts of these metals, gives an immediate white precipitate with barium salts; a similar precipitate after a short interval with strontium salts; and occasions no change with calcium salts. The precipitates with barium and strontium salts are insoluble in nitric acid.

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* Graham's Elements, vol. i. p. 593. For other methods see Watts's Dictionary of Chemistry, i. p. 904.

Solution of *calcium sulphate* gives an instantaneous cloud with barium salts, and one with strontium salts after a little time.

Strontium sulphate is itself sufficiently soluble to occasion turbidity when mixed with barium chloride.

Lastly, the soluble *oxalates* give, in the most dilute solutions of calcium salts, a white precipitate, which is not dissolved by a drop or two of hydrochloric, or by an excess of acetic acid. This is an exceedingly characteristic test.

The *chlorides of strontium* and *calcium* dissolved in alcohol, colour the flame of the latter red or purple: *barium salts* communicate to the flame a pale green tint.

Silicofluoric acid gives a white precipitate with barium salts, none with salts of strontium or calcium.

APPENDIX TO GROUP I.

METALS OF THE EARTHS.

THE metals belonging to this group are beryllium, yttrium, erbium, lanthanum, didymium, cerium, aluminium, zirconium, and thorinum. Beryllium is a dyad; yttrium, erbium, lanthanum, didymium, and cerium (in the cerous compounds), have hitherto been regarded as dyads; but recent observations have shown that they are more probably triads. Aluminium is also a triad; zirconium and thorinum are tetrads. All these metals form oxides of earthy character.

ALUMINIUM.

Atomic weight, 27·4. Symbol, Al.

THIS metal occurs very abundantly in nature in the state of silicate, as in felspar and its associated minerals; also in the various modifications of clay thence derived. It was first isolated by Wöhler, who obtained it as a grey powder by decomposing aluminium chloride with potassium; and H. Sainte-Claire Deville, by an improved process founded on the same principle, has succeeded in obtaining it in the compact form and on the manufacturing scale. The process consists in decomposing the double chloride of aluminium and sodium, $AlCl_3.NaCl$, by heating it with metallic sodium, fluor-spar or cryolite being added as a flux. The reduction is effected in crucibles, or on the large scale on the hearth of a reverberatory furnace. Sodium is used as the reducing agent in preference to potassium: first, because it is more easily prepared; and, secondly, because it has a lower atomic weight, and, consequently, a smaller quantity of it suffices to do the same amount of chemical work.

Aluminium is also prepared directly from cryolite by reduction with sodium, but the metal thus obtained is said to be more contaminated with iron and silicium than that prepared by Deville's process.

Aluminium is remarkable for its low specific gravity, which is 2·6 : it is nearly as white as silver, and is capable of assuming a high polish. It is employed in the manufacture of delicate apparatus and ornamental articles. Some of the alloys of aluminium promise to become more generally applicable, more especially the alloy with copper, which is remarkable for being similar in appearance to gold: this alloy is found in commerce under the name of aluminium bronze.

Aluminium forms only one class of compounds, in which it is trivalent, one atom of the metal being equivalent to three atoms of hydrogen ; thus the chloride is $AlCl_3$, the oxide, Al_2O_3, &c.

Aluminium Chloride, $AlCl_3$—This compound is obtained in solution by dissolving alumina or aluminium hydrate in hydrochloric acid; but the solution, when evaporated, gives off hydrochloric acid and leaves alumina. The anhydrous chloride may be prepared by heating a mixture of alumina and finely divided carbon in chlorine gas.

Pure precipitated alumina is dried and mixed with oil and lampblack, and the mixture, after being strongly calcined in a covered crucible, is introduced into a porcelain tube or tubulated earthen retort placed in a furnace, and connected at one end with an apparatus for evolving chlorine, and at the other with a dry receiver. On raising the heat to bright redness, and passing chlorine through the apparatus, aluminium chloride distils over, together with carbon monoxide, and condenses as a solid mass in the receiver :

$$Al_2O_3 + C_3 + Cl_6 = 2AlCl_3 + 3CO.$$

Aluminium chloride is a transparent waxy substance, having a crystalline structure, colourless when pure, but generally exhibiting a yellow colour, due perhaps to the presence of iron. It boils at about 180°, fumes in the air, and smells of hydrochloric acid. It is very deliquescent, and dissolves readily in water ; the solution when left to evaporate yields the hydrated chloride, $AlCl_3.6H_2O$, in six-sided prisms, which when heated are resolved into alumina and hydrochloric acid.

Aluminium and Sodium Chloride, $AlCl_3.NaCl$, is obtained by melting together the component chlorides in proper proportions, or by adding the requisite quantity of sodium chloride to the mixture of alumina and charcoal used for the preparation of aluminium chloride, igniting the mass in chlorine or hydrochloric acid, and condensing the vapour in a receiver. It is a crystalline mass, less deliquescent than aluminium chloride, and, therefore, more convenient for the preparation of aluminium.

Aluminum Fluoride, AlF_3, is produced by the action of gaseous silicon fluoride on aluminium, and forms cubic crystals, volatilising at a red heat, insoluble in water, and resisting the action of all acids.

Aluminium and Sodium Fluoride, $AlF_3.3NaF$, occurs abundantly as cryolite, at Evigtok in Greenland, and is prepared artificially by pouring hydrofluoric acid in excess on a mixture of calcined alumina and sodium carbonate. Cryolite forms quadratic crystals, colourless, transparent, softer than felspar, and of specific gravity 2·96. It is used, as already mentioned, for the preparation of aluminium, and in Germany for the manufacture of soda for the use of soap-boilers.

Aluminium Oxide.—Alumina, Al_2O_3.—This substance is inferred to be a sesquioxide from its isomorphism with ferric oxide. It is prepared by mixing a solution of alum with excess of ammonia, by which an extremely bulky, white, gelatinous precipitate of aluminium hydrate is thrown down. This is washed, dried, and ignited to whiteness. Thus obtained, alumina constitutes a white, tasteless, coherent mass, very little acted upon by acids. It is fusible before the oxy-hydrogen blowpipe. The mineral called *corundum*, of which the ruby and sapphire are transparent varieties, consists of nearly pure alumina in a cystallised state, with a little colouring oxide : emery, used for polishing glass and metals, is a coarse variety of corundum. Alumina is a very feeble base, and its salts have often an acid reaction.

Aluminium Hydrates.—Aluminium forms three hydrates; namely :—

Monohydrate, . . .	$AlHO_2$ or $Al_2O_3 . H_2O$
Dihydrate, ...	$Al_2H_4O_5$ or $Al_2O_3 . 2H_2O$
Trihydrate, ...	AlH_3O_3 or $Al_2O_3 . 3H_2O$.

The monohydrate is found native, as *diaspore*, in translucent masses which crumble to powder when heated, and give off the whole of their water at 360°.

The *trihydrate* is the ordinary gelatinous precipitate obtained by treating solutions of aluminium-salts—alum, for example—with ammonia or alkaline carbonates. When dried at a moderate heat, it forms a soft friable mass, which adheres to the tongue and forms a stiff paste with water, but does not dissolve in that liquid. At a strong red heat, it gives off water, and undergoes a very great contraction of volume. It dissolves with great facility in acids, and in the fixed caustic alkalis. When a solution of alumina in caustic potash is exposed to the air, the potash absorbs carbonic acid, and the aluminium trihydrate is then deposited in white crystals, which are but sparingly soluble in acids.

Aluminium trihydrate has a very powerful attraction for organic matter, and when digested in solutions of vegetable colouring matter, combines with and carries down the colouring matter, which is thus removed entirely from the liquid if the alumina is in sufficient quantity. The pigments called *lakes* are compounds of this nature. The fibre of cotton impregnated with alumina acquires the same power of retaining colouring matters : hence the great use of aluminous salts as *mordants* to produce fast colours.

Aluminium trihydrate occurs native as *Gibbsite*, a stalactitic, translucent, fibrous mineral, easily dissolved by acids.

Dihydrate.—When a dilute solution of aluminium diacetate is exposed for several days to a temperature of 100° in a close vessel, the acetic acid appears to be set free, although no precipitation of alumina takes place. The liquid acquires the taste of acetic acid, and if afterwards boiled in an open vessel, gives off nearly the whole of its acetic acid, the alumina, nevertheless, remaining in solution. This solution is coagulated by mineral acids and by most vegetable acids, by alkalis, and by decoctions of dye-woods. The alumina contained in it is, however, no longer capable of acting as a mordant. Its coagulum with dye-woods has the colour of the infusion, but is translucent and totally different from the dense opaque lakes which ordinary alumina forms with the same colouring matters. On evaporating the solution to dryness at 100°, the alumina remains in the form of dihydrate, retaining only a trace of acetic acid. In this state it is insoluble in the stronger acids, but soluble in acetic acid, provided it has not been previously coagulated in the manner just mentioned. Boiling potash converts it into the trihydrate.*

Aluminates.—The hydrogen in aluminium trihydrate may be replaced by an equivalent quantity of various metals; such compounds are called *aluminates.* According to Frémy, a solution of alumina in potash slowly evaporated, out of contact with the air, deposits granular crystals of potassium aluminate, $AlKO_2$, or $Al_2O_3.K_2O$. Similar compounds occur native; thus *Spinell* is an aluminate of magnesium, Al_2MgO_4; *Gahnite*, an aluminate of zinc, Al_2ZnO_4.

Aluminium Sulphide, Al_2S_3.—When the vapour of carbon bisulphide is passed over alumina, at a bright red heat, a glassy melted mass remains, which is instantly decomposed by water, with evolution of sulphuretted hydrogen.

Aluminium Sulphate, $Al_2(SO_4)_3.18H_2O$, or $Al_2O_3.3SO_3.18H_2O$.—Prepared by saturating dilute sulphuric acid with aluminium hydrate, and evaporating; or, on the large scale, by heating clay with sulphuric acid. It crystallises in thin pearly plates, soluble in 2 parts of water: it has a sweet and astringent taste, and an acid reaction. Heated to redness, it is decomposed, leaving pure alumina. Two other aluminium sulphates, with excess of base, are also described, one of which is insoluble in water.

Aluminium sulphate combines with the sulphates of potassium, sodium, and ammonium, and the other alkali-metals, forming double salts of great interest, the *alums.* Common alum, the source of all the preparations of alumina, contains $AlK(SO_4)_2.12H_2O$. It is manufactured on a very large scale from a kind of slaty clay loaded with iron bisulphide, which abounds in certain localities. This is gently roasted, and then exposed to the air in a moistened state; oxygen is absorbed; the sulphur becomes acidified; ferrous sulphate and aluminium sulphate are produced, and afterwards separated by lixiviation with water. The solution is next concentrated, and mixed with a quantity of potassium chloride, which decomposes the iron-salt, forming ferrous chloride and potassium sulphate: the latter combines with the aluminium sulphate to form alum. By crystallisation the alum is separated from the highly soluble iron chloride, and afterwards easily purified by a repetition of the process. Other methods of alum making are sometimes employed.

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* Walter Crum, Chem. Soc. Journ. vi. 225.

Potassium-alum crystallises in colourless, transparent octohedrons which often exhibit the faces of the cube. It has a sweetish and astringent taste, reddens litmus-paper, and dissolves in 18 parts of water at 15·5°, and in its own weight of boiling water. Exposed to heat, it is easily rendered anhydrous, and by a very high temperature it is decomposed. The crystals have little tendency to change in the air. Alum is largely used in the arts, in preparing skins, dyeing, &c.: it is occasionally contaminated with iron oxide, which interferes with some of its applications. The celebrated Roman alum, made from *alum-stone*, a felspathic rock altered by sulphurous vapours, was once much prized on account of its freedom from this impurity. A mixture of dried alum and sugar, carbonised in an open pan, and then heated to redness in a glass flask, contact with air being avoided, furnishes the *Homberg's pyrophorus*, which ignites spontaneously on exposure to the air. The essential ingredient is, in all probability, finely divided potassium sulphide.

A process has lately been patented by Messrs. Duncan and Newlands for separating the potash from syrups of beet and cane sugar by means of aluminium sulphate, the potash being thereby precipitated in the form of alum. A solution of aluminium sulphate of a density corresponding with about 27° of Baume's hydrometer is added to the cold syrup having a density of about 36° B., in quantity sufficient to precipitate the whole of the potash present; the mixture is well stirred for fifteen minutes to an hour; and the whole left at rest for four or five hours till the deposit has completely subsided. This deposit consists of small crystals, technically known as "alum meal." Considerable quantities of alum are now made by this process.

Sodium-alum, in which sulphate of sodium replaces sulphate of potassium, has a form and constitution similar to that of common alum: it is, however, much more soluble, and difficult to crystallise.

Ammonium-alum, containing NH_4 instead of K, very closely resembles common potassium alum, having the same figure, appearance, and constitution, and nearly the same degree of solubility as that substance. It is manufactured for commercial use. As the value of potassium salts is continually increasing, ammonium-alum, which may be used in dyeing with the same advantage as the corresponding potassium salt, has almost entirely replaced the potassium-alum. When heated to redness, ammonium-alum yields pure alumina.

Cæsium-alum, $AlCs(SO_4)_2.12H_2O$, and *Rubidium-alum*, $AlRb(SO_4)_2.12H_2O$, resemble potassium alum. A *silver-alum*, $AlAg(SO_4)_2.12H_2O$, is formed by heating equivalent quantities of argentic and aluminium sulphates till the former is dissolved. It crystallises in regular octohedrons, and is resolved by water into its component salts. There is also a *thallium alum*, $AlTh(SO_4)_2.12H_2O$, which crystallises in regular octohedrons.

Lastly, there are alums isomorphous with those just described, in which the trivalent aluminium is replaced by trivalent iron, chromium, and manganese: for example, potassio-ferric sulphate or potassium-iron alum, $FeK(SO_4)_2.12H_2O$; *ammonio-chromic sulphate*, $Cr(NH_4)(SO_4)_2.12H_2O$. These will be described further on.

Few other aluminium salts present especial interest, except the silicates; but these latter are of great importance. Silicates of aluminium enter into the composition of a number of crystallised minerals, among which felspar, by reason of its abundant occurrence, occupies a prominent place. Granite, porphyry, trachyte, and other ancient unstratified rocks, consist in great part of this mineral, which, under peculiar circumstances, by no means well understood, and particularly by the action of the carbonic acid of the air, suffers complete decomposition, being converted into a soft, friable mass of earthy matter. This is the origin of clay: the change itself is seen in great perfection in certain districts of Devonshire and Cornwall, the felspar of the fine white granite of those localities being often disintegrated to a great depth, and the rock altered to a substance resembling soft mortar. By washing, this finely divided matter is separated from the quartz and mica; and the milk-like liquid, being stored up in tanks, deposits the suspended clay, which is afterwards dried, first in the air, and afterwards in a stove, and employed in the manufacture of porcelain. The composition assigned to unaltered felspar is $AlKSi_3O_8$, or $AlKSiO_4.2SiO_2$, or $Al_2O_3.K_2O.6SiO_2$. The exact nature of the change by which felspar passes into porcelain clay is unknown, although it evidently consists in the abstraction of silica and alkali.

When the decomposing rock contains iron oxide, the clay produced is coloured. The different varieties of shale and slate result from the alteration of ancient clay-beds, apparently in many instances by the infiltration of water holding silica in solution: the dark appearance of some of these deposits is due to bituminous matter.

It is a common mistake to confound clay with alumina: all clays are essentially silicates of that base; they often vary a good deal in composition. Dilute acids exert little action on these compounds; but by boiling with oil of vitriol, alumina is dissolved out, and finely divided silica left behind. Clays containing an admixture of calcium carbonate are termed *marls*, and are recognised by effervescing with acids.

A basic aluminium silicate, $Al_2O_3.SiO_2$, is found crystallised, constituting the beautiful mineral called *cyanite*. The compounds formed by the union of the aluminium silicates with other silicates are almost innumerable. A sodium felspar, *albite*, containing that metal in place of potassium, is known, and there are two somewhat similar lithium compounds, *spodumene* and *petalite*. The *zeolites* are hydrated silicates belonging to this class; *analcime*, *nepheline*, *mesotype*, &c., are double silicates of sodium and aluminium, with

[illegible], is disting
Caustic *potash* and *soda* occasion a white
aluminium hydrate, freely soluble in exces
produces a similar precipitate, insoluble
The *alkaline carbonates* and *carbonate of*
hydrate, with escape of carbonic acid
insoluble in excess.

Ammonium sulphide also produces
aluminium hydrate.

BERYLLIUM, or GLU

Atomic weight, 9·4. Symb

This somewhat rare metal occurs as a sil
phenacite, or associated with other silica
euclase, leucophane, helvite, and several var
as an aluminate in chrysoberyl or cymophan

Metallic beryllium is obtained by passi
chloride over melted sodium. It is a white
2·1; it may be forged and rolled into sheets
point is below that of silver. It does not
boiling heat. Sulphuric and hydrochloric
evolution of hydrogen.

Beryllium forms but one class of compo
siderable doubt as to its atomic weight and
the one hand, it is regarded as a dyad, like
with the atomic weight 9·4, its chloride bein
on the other hand, as a triad, like aluminiu
its chloride would be $BeCl_3$, its oxide Be_2O_3
14; but the former view appears. on the
accordance

finely pounded mineral with potassium carbonate or quicklime; treating the fused mass with hydrochloric acid; evaporating to dryness; then moistening the residue with hydrochloric acid, and treating it with water, whereby everything is dissolved except the silica. The filtered liquid is then mixed with excess of ammonia solution, which throws down a bulky precipitate containing both alumina and beryllia; this precipitate is well washed, and the beryllia is dissolved out from the alumina by digestion in a cold strong solution of ammonium carbonate. The liquid is again filtered, and on boiling it, beryllium carbonate is deposited as a white powder, which, when ignited, leaves pure beryllia.

Beryllia is very much like alumina in physical characters, and further resembles that substance in being readily dissolved by caustic potash or soda; but it is distinguished from alumina by its solubility, when recently precipitated, in a cold solution of ammonium carbonate. Beryllium salts have a sweet taste, whence the former name of the metal, *glucinum* (from γλυκύς). They are colourless, and are distinguished from those of aluminium by not yielding an alum with potassium sulphate, nor a blue colour when heated before the blowpipe with cobalt nitrate; also by their reaction with ammonium carbonate.

ZIRCONIUM.

Atomic weight, 89·6. Symbol, Zr.

THIS is a tetrad metal, intermediate in many of its properties between aluminium and silicium. Its oxide, zirconia, was first obtained by Klaproth, in 1789, from zircon, which is a silicate of zirconium. It has since been found in fergusonite, eudialyte, and two or three other rare minerals.

Zirconium, like silicon, is capable of existing in three different states, amorphous, cystalline, and graphitoïdal. The amorphous and crystalline varieties are obtained by processes similar to those described for preparing the corresponding modifications of silicium; graphitoïdal zirconium was obtained, by Troost, in attempting to decompose sodium zirconate with iron, in light scales of a steel-grey colour. Amorphous zirconium when heated in the air takes fire at a heat somewhat below redness, and burns with a bright light forming zirconia. Crystalline zirconium forms very hard brittle scales resembling antimony in colour and lustre; it burns in the air only at the heat of the oxy-hydrogen blowpipe, but takes fire at a red heat in chlorine gas. Zirconium is but little attacked by the ordinary acids; but hydrofluoric acid dissolves it readily, with evolution of hydrogen.

Zirconium Oxide, or **Zirconia**, ZrO_2, is prepared by strongly igniting zircon (zirconium silicate), with four times its weight of dry sodium carbonate and a small quantity of sodium hydrate. The silica is separated from the fused mass by hydrochloric acid, as described in the case of beryllia; the resulting solution is treated with ammonia, which throws down zirconia generally mixed with ferric oxide; the precipitate is redissolved in hydrochloric acid; and the solution is boiled with excess of sodium thiosulphate as long as sulphurous acid continues to escape, whereby pure zirconia is precipitated, the whole of the iron remaining in the solution. Zirconia thus obtained forms a white powder, or hard lumps, of specific gravity 4·35 to 4·9. By fusing it with borax in a pottery furnace and dissolving out the soluble salts with hydrochloric acid, zirconia is obtained in small quadratic prisms isomorphous with the native oxides of tin and titanium.

Zirconium hydrates are obtained by precipitating the solution of a zirconium salt with ammonia; the precipitate contains $ZrH_2O_3 = ZrO_2.H_2O$, or $ZrH_4O_4 = ZrO_2.2H_2O$, according to the temperature at which it is dried.

Zirconia acts both as a base and as an acid. After ignition it is insoluble in all acids except hydrofluoric and very strong sulphuric acid, but the hydrate dissolves easily in acids, forming the zirconium salts; the normal sulphate has the composition $Zr(SO_4)_2$, or $ZrO_2.2SO_3$.

Compounds of zirconia with the stronger bases, called zirconates, are obtained by precipitating a zirconium salt with potash or soda, or by igniting zirconia with an alkaline hydrate. *Potassium zirconate* dissolves completely in water. Three *sodium zirconates* have been formed, containing $Na_2ZrO_3 = Na_2O.ZrO_2$; $Na_4ZrO_4 = 2Na_2O.ZrO_2$; and $Na_2Zr_8O_{17} = Na_2O.8ZrO_2$.

Zirconium Fluoride, ZrF_4.—This compound is obtained by dissolving zirconia, or the hydrate, in hydrofluoric acid; or in the anhydrous state, by igniting zirconia with ammonium and hydrogen fluoride till all the ammonium fluoride is driven off. It unites with other metallic fluorides, forming double salts, called zircofluorides or fluozirconates, which are isomorphous with the corresponding silicofluorides, stannofluorides, and titanofluorides, and are mostly represented by the formulæ—

$$4MF.ZrF_4;\quad 3MF.ZrF_4;\quad 2MF.ZrF_4;\quad MF.ZrF_4,$$

in which M denotes a monad metal. The sodium salt, however, has the composition $5NaF.3ZrF_4$.

THORINUM, or THORIUM.

Atomic weight, 231·5. Symbol, Th.

THIS very rare metal was discovered in 1828 by Berzelius, in thorite, a mineral from the Norwegian island Lovön, in which it exists as a silicate. It has since been found in euxenite, pyrochlore, and a few other minerals, all very scarce.

Metallic thorinum is obtained by reducing the chloride with potassium or sodium, as a grey powder, which acquires metallic lustre by pressure, and has a density of 7·66 to 7·9. It is not oxidised by water, dissolves easily in nitric, slowly in hydrochloric acid, and is not attacked by caustic alkalis.

Thorinum forms but one class of compounds, in all of which it is quadrivalent.

Thorinum Oxide, or **Thorina**, ThO_2, is prepared by decomposing thorite with hydrochloric acid, separating the silica in the usual way, treating the filtered solution with hydrogen sulphide to separate lead and tin, and precipitating the thorina by ammonia, together with small quantities of the oxides of iron, manganese, and uranium. To get rid of these, the precipitate is redissolved in hydrochloric acid, and the hot saturated solution is boiled with a solution of neutral potassium sulphate. The thorinum is thereby precipitated as thorinum and potassium sulphate; and from the solution of this salt in hot water, the thorinum is precipitated by alkalis as a hydrate, which, on ignition, yields pure thorina.

Thorina is white, and very heavy, its specific gravity being 9·402. After ignition it is insoluble in nitric and hydrochloric acids, and dissolves in strong sulphuric acid only after prolonged heating. The *hydrate*, prcipitated from thorinum salts by alkalis, dissolves easily in acids.

Thorinum Chloride, $ThCl_4$, prepared by igniting an intimate mixture of thorina and charcoal in chlorine gas, sublimes in white shining crystals. It forms double salts with the chlorides of the alkali-metals.

Thorinum Sulphate, $Th(SO_4)_2$, crystallises with various quantities of water, according to the temperature at which its solution is evaporated. *Thorinum* and *potassium sulphate*, $ThK_4(SO_4)_4.2H_2O$, separates as a crystalline powder when a crust of potassium sulphate is suspended in a solution of thorinum sulphate. It is easily soluble in water, but insoluble in alcohol and in solution of potassium sulphate.

CERIUM.—LANTHANUM.—DIDYMIUM.

Ce = 138.—La = 139.—Di = 144·75.

THESE three metals occur together as silicates in the Swedish mineral cerite, also in allanite, orthite, and a few others; and as phosphates in monazite, edwardsite, and cryptolite, a mineral occurring disseminated through apatite and through certain cobalt ores.

Cerium was discovered in 1803 by Klaproth, and by Hisinger and Berzelius, who obtained it in the form of oxide from cerite. This mineral is completely decomposed by boiling with strong hydrochloric acid, silica being separated, and the cerium, together with iron and other metals, dissolving as chloride. On treating the acid solution thus obtained with oxalic acid, cerium oxalate is precipitated as a white crystalline powder, which, when ignited, leaves a brown oxide. The product thus obtained was for some time regarded as the oxide of a single metal, **cerium**; but in 1839 and 1841, Mosander* showed that it contained the oxides of two other metals, which he designated as **lanthanum**† and **didymium**.‡

Cerium oxide may be separated from the oxides of lanthanum and didymium by treating the crude brown oxide above mentioned, first with dilute and then with strong nitric acid, which gradually removes the whole of the lanthanum and didymium oxides.

The separation of these two oxides one from the other is much more difficult, and can be effected only by successive crystallisation of their sulphates. If the lanthanum salt is in excess, in which case the solution of the mixed sulphates has only a faint amethyst tinge, the liquid is evaporated to dryness, and the residue heated to a temperature just below redness, to render the sulphates anhydrous. The residue thus obtained is then to be added by small portions to ice-cold water, which dissolves it easily, and the resulting solution heated in a water-bath to about 40°. Lanthanum sulphate then crystallises out, containing only a small quantity of didymium, and may be further purified by repeating the whole process. If, on the other hand, the didymium salt is in excess, in which case the liquid has a decided rose colour, separation may be effected by leaving the acid solution in a warm place for a day or two. Didymium sulphate then separates in large rhombohedral crystals.

Metallic cerium, lanthanum, and didymium are obtained by reducing the chlorides with sodium, in the form of grey powders, which decompose water at ordinary temperatures, and dissolve rapidly in dilute acids with evolution of hydrogen.

Atomic Weights and Quantivalence.—According to the atomic weights hitherto assigned to these three metals, viz.. Ce=92, La=93·6, Di=95 (see Table on page 2), lanthanum and didymium should be dyads, forming chlorides and oxides of the types RCl_2 and RO, and cerium should be classed with the iron-metals. Mendelejeff, however, as already observed, proposed to alter the atomic weights in accordance with the periodic law of the elements, making Di = 138 (triad), Ce=140, La=180 (tetrads). But according to recent determinations of the specific heats of these three metals, it would appear that in their most stable combinations they are all three triadic or trivalent. Hillebrand‖ finds for the specific heats the following values:—

Ce	La	Di
0·0479	0·04485	0·04653,

and Mendelejeff finds for cerium the number 0·050. Now these numbers, multiplied by the hitherto received atomic weights of the respective metals, give for the atomic heats the values 4·12, 4·15, and 4·40, which do not agree with the law of Dulong and Petit (p. 248); but if these atomic weights are increased in the ratio of 2 to 3, which amounts to making their lower oxides sesquioxides R_2O_3 instead of monoxides RO, their values, with small corrections, according to recent analyses by Hillebrand, become

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* Poggendorff's Annalen, xlvi. 648; xlvii. 207; lvi. 504.

† From λανθάνειν, to lie hid.

‡ From δίδυμοι, twins.

‖ Poggendorff's Annalen (1876), clxiii. 71.

Ce	La	Di
138	139	144·75,

giving for the atomic heats, the values

6·18 6·23 6·60,

which are in accordance with the general law.

Cerium forms two series of compounds, viz., the cerous compounds, in which it is trivalent, as above stated, *e.g.*, $CeCl_3$, Ce_2O_3, $Ce_2(SO_4)_3$; and the ceric compounds in which it is quadrivalent, *e.g.*, ceric oxide, CeO_2 [formerly ceroso-ceric oxide Ce_3O_4], ceric sulphate $Ce(SO_4)_2$ * &c. There are also two fluorine-compounds of cerium, in which it appears to have still higher equivalent values.

Cerous oxide, Ce_2O_3, is obtained by igniting the carbonate or oxalate in a current of hydrogen, as a greyish-blue powder, quickly converted into ceric oxide on exposure to the air. Its salts are colourless. The *sulphate*, $Ce_2(SO_4)_3$, crystallises with various quantities of water, according to the temperature at which it is deposited. *Cerium and potassium sulphate*, $CeK_3(SO_4)_3$, separates as a white powder on immersing solid potassium sulphate in a solution of a cerous salt. It is slightly soluble in pure water, but insoluble in a saturated solution of potassium sulphate. The formation of this salt affords the means of separating cerium from most other metals.

Ceric oxide, CeO_2, is produced when cerous hydrate, carbonate, or nitrate is ignited in an open vessel. It is yellowish-white, acquires a deep orange-red colour when heated, but recovers its original tint on cooling. It is not converted into a higher oxide by ignition in oxygen. *Ceric hydrate*, $2CeO_2.3H_2O$, obtained by passing chlorine into aqueous potash in which cerous hydrate is suspended, is a bright yellow precipitate, which dissolves readily in sulphuric and nitric acids, forming yellow solutions of ceric salts; and in hydrochloric acid, with evolution of chlorine, forming colourless cerous chloride.

The solution of the sulphate yields by spontaneous evaporation, first, brown-red crystals of a *ceroso-ceric salt*, $\left.\begin{matrix}Ce_2(SO_4)_3\\2Ce(SO_4)_2\end{matrix}\right\} + 4\,aq.$, and afterwards yellow indistinctly crystalline *ceric sulphate*, $Ce(SO_4)_2.4\,aq.$

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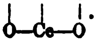
* If these formula be doubled, the ceric compounds may also be regarded as containing trivalent cerium, *e.g.*, Ce_2O_4 or



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Lanthanum forms only one set of comp
$La_2(SO_4)_3$. There is, however, a higher
which is not exactly known. Lanthanum
solutions yield, with alkalis, a precipitate
LaH_3O_3, which, when ignited, leaves the
oxide. Both the hydroxide and the anhyd
in acids. *Lanthanum sulphate* forms small p
ing $La_2(SO_4)_3.9H_2O$. *Lanthanum and potas*
is formed, on mixing the solution of a lanth
sulphate, as a white crystalline precipitat
sponding cerium salt.

Didymium salts are rose-coloured, and
alkalis, a pale rose-coloured precipitate of
which, when ignited in a covered crucibl
monoxide, Di_2O_3, in white, hard lumps.
hydroxide, nitrate, carbonate, or oxalate of
contact with the air, and not very strongly
is left, containing from 0·8 to 0·9 per cent
monoxide. This, when treated with acids,
off oxygen and yielding a salt of the monox

Didymium sulphate separates from an acid
evaporation, in well-defined rhombohed
numerous secondary faces, and containing
isomorphous with the similarly constitute
and erbium. The sulphate is more
in hot water, and a solution saturated
when heated to the boiling-point, a crys
ing $Di_2(SO_4)_3$. 6 aq.

Didymium and potassium sulphate, DiK

YTTRIUM AND ERBIUM.

Y=92. Eb=168·9.

THESE metals exist as silicates in the gadolinite or ytterbite of Ytterby in Sweden, and in a few other rare minerals. A third metal, called terbium, has also been supposed to be associated with them ; but recent experiments, especially those of Bahr and Bunsen,* have thrown very great doubt upon its existence.

To obtain the earths, yttria and erbia, in the separate state, gadolinite is digested with hydrochloric acid, and the solution separated from the silica is treated with oxalic acid, which throws down the oxalates of erbium and yttrium, together with those of calcium, cerium, lanthanum, and didymium. These oxalates are converted into nitrates ; the solution is treated with excess of solid potassium sulphate, to separate the cerium metals ; the erbium and yttrium, which still remain in solution, are again precipitated by oxalic acid ; and the same treatment is repeated, till the solution of the mixed earths, when examined by the spectral apparatus, no longer exhibits the absorption-bands characteristic of didymium. To separate the erbia and yttria, they are again precipitated by oxalic acid. The oxalates are converted into nitrates, and the nitrates of erbium and yttrium are separated by a series of fractional crystallisations, the erbium salt being the less soluble of the two, and crystallising out first ; but the process requires attention to a number of details, which cannot be here described †

Metallic erbium has not been isolated. Yttrium (containing erbium) was obtained by Berzelius, as a blackish grey powder, by igniting yttrium chloride with potassium.

Yttrium and erbium have hitherto been regarded as dyads, with the atomic weights Y=61·7, Eb=112·6; but the close analogy of their compounds to those of lanthanum and didymium renders it more probable that they are triads, with the higher atomic weights above given. In the absence, however, of exact determinations of the specific heats of these metals, the question must for the present be regarded as undecided.

Erbia, Eb_2O_3, obtained by ignition of erbium nitrate or oxalate, has a faint rose colour. It does not melt at the strongest white heat, but aggregates to a spongy mass, glowing with an intense green light, which, when examined by the spectroscope, exhibits a *continuous* spectrum intersected by a number of bright bands. Solutions of erbium-salts, on the other hand, give an absorption-spectrum exhibiting dark bands, and *the points of maximum intensity of the light bands in the emission-spectrum of glowing erbia coincide exactly in position with the points of greatest darkness in the absorp-*

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* Ann. Ch. Pharm. cxxxvii. 1.

† See Watts's Dictionary of Chemistry, vol. v. p. 721.

tion spectrum. The position of these bands is totally different from those in the emission and absorption-spectra of didymium.*

Erbium salts have a rose-red colour, deeper in the hydrated than in the anhydrous state; they have an acid reaction and sweet astringent taste. The *sulphate*, $3EbSO_4.8$ aq., forms light rose-coloured crystals, isomorphous with the sulphates of yttrium and didymium.

Yttria, Y_2O_3, is a soft, nearly white powder, which when ignited glows with a pure white light, and yields a spectrum not containing any bright bands, like that of erbia. It does not unite directly with water, but is precipitated as a hydrate by alkalis, from solutions of yttrium-salts. It dissolves slowly but completely in hydrochloric, nitric, and sulphuric acids, forming colourless solutions, which do not exhibit an absorption-spectrum.

Yttrium sulphate, $Y_2(SO_4)_3.8$ aq., forms small colourless crystals.

Reactions of the Earth-metals.

1. All these metals are precipitated from their solutions by ammonium sulphide, as hydrates, not as sulphides. They are not precipitated by hydrogen sulphide.

2. The hydrates of aluminium and beryllium are soluble in *caustic potash*; those of the other earth-metals are insoluble.

3. Beryllium hydrate dissolves in a cold saturated solution of *ammonium carbonate*, and is precipitated, as carbonate, on boiling. Aluminium hydrate is insoluble in ammonium carbonate (see further, p. 395).

4. Of the earth-metals whose hydrates are insoluble in potash,—namely, zirconium, thorinum, cerium, lanthanum, didymium, erbium, and yttrium,—zirconium and thorinum may be precipitated as thiosulphates by boiling the solution with *sodium thiosulphate*, the other metals remaining in solution. The precipitate when ignited leaves pure zirconia and thorina, or a mixture of the two.

5. Zirconium and thorinum may be separated one from the other by means of *ammonium oxalate*, which, when added in excess, precipitates the thorinum as oxalate, and leaves the zirconium in solution.

6. Cerium, lanthanum, and didymium are separated from yttrium and erbium by adding an excess of *potassium sulphate*, which throws down the cerium metals, leaving yttrium and erbium in solution; to ensure complete precipitation, the solution must be left in contact for some time with a piece of solid potassium sulphate.

Cerium may be separated from lanthanum and didymium, as already observed, by treating the mixed oxides several times with *nitric acid* (p. 398). Another method is to boil the mixed oxides (the cerium being in the state of ceric oxide) with solution of *sal-ammoniac*. The lanthanum and didymium then gradually dissolve, as chlorides, while the cerium remains as ceric oxide. A third method is to precipitate the solution of the three metals with excess of potash, and pass *chlorine* in excess through the solution and precipitate; the cerium is then separated as bright yellow ceric hydrate, while the lanthanum and didymium redissolve as chlorides. This reaction serves to detect very small quantities of cerium mixed with the other two metals. Cerium is further distinguished by the light-yellow colour of anhydrous ceric oxide, and by the reaction of its compounds, when fused before the blowpipe with borax or phosphorus salt, the glass thus formed being deep red while hot, and becoming colourless on cooling. Didymium is distinguished by the dark-brown colour of its higher oxide; by the pale rose-colour which its salts impart to a bead of borax or phosphorus salt; and by the peculiar character of its absorption-spectrum (p. 400).

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* The paper by Bahr and Bunsen, above referred to, is accompanied by exact diagrams of the erbium and didymium spectra.

The methods of separating lanthanum from didymium, and yttrium from erbium—imperfect at the best—have been already noticed.

MANUFACTURE OF GLASS, PORCELAIN, AND EARTHENWARE.

Glass.—Glass is a mixture of various insoluble silicates with excess of silica, altogether destitute of crystalline structure; the simple silicates, formed by fusing the bases with silicic acid in equivalent proportions, very often crystallise, which happens also with the greater number of the natural silicates included among the earthy minerals. Compounds identical with some of these are also occasionally formed in artificial processes, where large masses of melted glassy matter are suffered to cool slowly. The alkaline silicates, when in a state of fusion, have the power of dissolving a large quantity of silica.

Two principal varieties of glass are met with in commerce, namely, glass composed of silica, alkali, and lime; and glass containing a large proportion of lead silicate: *crown* and *plate glass* belong to the former division; *flint glass*, and the material of artificial gems, to the latter. The lead promotes fusibility, and confers also density and lustre. Common green bottle-glass contains no lead, but much silicate of iron, derived from the impure materials. The principle of the glass manufacture is very simple. Silica, in the shape of sand, is heated with potassium or sodium carbonate, and slaked lime or lead oxide; at a high temperature, fusion and combination occur, and the carbonic acid is expelled. Glauber's salt mixed with charcoal is sometimes substituted for soda. When the melted mass has become perfectly clear and free from air-bubbles, it is left to cool until it assumes the peculiar tenacious condition proper for working.

The operation of fusion is conducted in large crucibles of refractory fire-clay, which in the case of lead-glass are covered by a dome at the top, and have an opening at the side, by which the materials are introduced, and the melted glass withdrawn. Great care is exercised in the choice of the sand, which must be quite white and free from iron oxide. Red lead, one of the higher oxides, is preferred to litharge, although immediately reduced to monoxide by the heat, the liberated oxygen serving to destroy any combustible matter that might accidentally find its way into the crucible, and stain the glass by reducing a portion of the lead. Potash gives a better glass than soda, although the latter is very generally employed, from its lower price. A certain proportion of broken and waste glass of the same kind is always added to the other materials.

Articles of blown glass are thus made: The workman begins by collecting a proper quantity of soft pasty glass at the end of his *blowpipe*, an iron tube five or six feet in length, terminated by a mouthpiece of wood; he then begins blowing, by which the lump is expanded into a kind of flask, susceptible of having its form modified by the position in which it is held, and the velocity of rotation continually given to the iron tube. If an open-mouthed vessel is to be made, an iron rod, called a *pontil* or *puntil*, is dipped into the glass pot and applied to the bottom of the flask, to which it thus serves as a handle, the blowpipe being removed by the application of a cold iron to the neck. The vessel is then reheated at a hole left for the purpose in the wall of the furnace, the aperture enlarged, and the vessel otherwise altered in figure by the aid of a few simple tools, until completed. It is then detached, and carried to the annealing oven, where it undergoes slow and gradual cooling during many hours, the object of which is to obviate the excessive brittleness always exhibited by glass which has been quickly cooled. The large circular *tables* of crown glass are made by a very curious process of this kind; the globular flask at first produced, transferred from the blowpipe to the pontil, is suddenly made to assume the form of a flat disc by the centrifugal force of the rapid rotatory movement given to the rod. Plate glass is cast upon a flat metal table, and, after very careful annealing, ground true and polished by suitable machinery. Tubes are made by rapidly drawing out a hollow cylinder; and from these a great variety of useful small apparatus may be constructed with the help of a lamp and blowpipe, or, still better, the bellows table of the barometer-maker. Small tubes may be bent in the flame of a spirit-lamp or gas-jet, and cut with great ease by a file, a scratch being made, and the two portions pulled or broken asunder in a way easily learned by a few trials.

Specimens of the two chief varieties of glass gave the following results on analysis:—

Bohemian plate glass (excellent).		English flint glass.	
Silica,	60·0	Silica,	51·93
Potassium oxide,	25·0	Potassium oxide,	13·77
Lime,	12·5	Lead oxide,	33·28
	97·5		99·98

The difficultly fusible white Bohemian tube, so valuable in organic analysis, has been found to contain, in 100 parts—

Silica, ...	72·80
Lime, with trace of alumina, . . .	9·68
Magnesia, ...	·40
Potassium oxide, ...	16·80
Traces of manganese, &c., and loss, . .	·32

Different colours are often communicated to glass by metallic oxides. Thus, oxide of cobalt gives deep blue; oxide of manganese, amethyst; cuprous oxide, ruby-red; cupric oxide, green; the oxides of iron, dull green or brown, &c. These are either added to the melted contents of the glass-pot, in which they dissolve, or applied in a particular manner to the surface of the plate or other object, which is then reheated, until fusion of the colouring matter occurs: such is the practice of enamelling and glass-painting. An opaque white appearance is given by oxide of tin; the enamel of watch-faces is thus prepared.

Toughened Glass.—When ordinary glass is heated till it begins to soften, then plunged into melted paraffin, wax, or other substance melting at a comparatively low temperature, and then left to cool gradually, it becomes very tough, so that it may be struck or thrown on the ground without breaking. It has also acquired greater power of resisting heat, and may be heated to redness, then dipped into cold water, and whilst wet again held in the flame, without injury. Hence it is well adapted for lamp-chimneys and for culinary vessels. When it does break, however, it splits up into a multitude of minute angular fragments, indicating a crystalline structure, the existence of which is confirmed by the appearance of the toughened glass in polarised light.

Soluble Glass.—When silica is melted with twice its weight of potassium or sodium carbonate, and the product treated with water, the greater part dissolves, yielding a solution from which acids precipitate gelatinous silica. This is *soluble glass* or *water glass;* its solution has been used for rendering muslin and other fabrics of cotton or linen less combustible, for making artificial stone, and preserving natural stone from decay, and for a peculiar style of mural painting called *stereochromy.*[*]

Porcelain and Earthenware.—The plasticity of natural clays, and their hardening when exposed to heat, are properties which suggested in very early times their application to the making of vessels for the various purposes of daily life: there are few branches of industry of higher antiquity than that exercised by the potter.

True porcelain is distinguished from earthenware by very obvious characters. In porcelain the body of the ware is very compact and translucent, and breaks with a conchoïdal fracture, symptomatic of a commencement of fusion. The glaze, too, applied for giving a perfectly smooth surface, is closely adherent, and, in fact, graduates by insensible degrees into the substance of the body. In earthenware, on the contrary, the fracture is open and earthy, and the glaze detachable with greater or less facility. The compact and partly glassy character of porcelain is the result of the admixture with the clay of a small portion of some substance such as felspar, or a calcic or alkaline silicate, which is fusible at the temperature to which the ware is exposed when baked or fired, and being absorbed by the less fusible portion, binds the whole into a solid mass on cooling. The clay employed in porcelain-making is always directly derived from decomposed felspar, none of the clays of the secondary strata being pure enough for the purpose: it must be white, and free from iron oxide. To diminish the contraction which this substance undergoes in the fire, a quantity of finely divided silica, carefully prepared by crushing and grinding calcined flints or chert, is added, together with a proper proportion of felspar or other fusible material, also reduced to impalpable powder. The utmost pains are taken to effect perfect uniformity of mixture, and to avoid the introduction of particles of grit, or other foreign bodies. The ware itself is fashioned either on the potter's wheel—a kind of vertical lathe—or in moulds of plaster of Paris, and dried first in the air, afterwards by artificial heat, and at length completely hardened by exposure to the temperature of ignition. The porous *biscuit* is now fit to receive its glaze, which may be either ground felspar, or a mixture of gypsum, silica, and a little porcelain clay, diffused through water. The piece is dipped for a moment into this mixture, and withdrawn; the water sinks into its substance, and the powder remains evenly spread upon its surface; it is once more dried, and, lastly, fired at an exceedingly high temperature.

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[*] See Richardson and Watts's Chemical Technology, vol. i. part iv. pp. 69–104.

The porcelain-furnace is a circular structure of masonry, having several fire-places, and surmounted by a lofty dome. Dry wood or coal is consumed as fuel, and its flame directed into the interior, and made to circulate around and among the earthen cases, or *seggars*, in which the articles to be fired are packed. Many hours are required for this operation, which must be very carefully managed. After the lapse of several days, when the furnace has completely cooled, the contents are removed in a finished state, so far as regards the ware.

The ornamental part, consisting of gilding and painting in enamel, has yet to be executed; after which the pieces are again heated, in order to flux the colours. The operation has sometimes to be repeated more than once.

The manufacture of porcelain in Europe is of modern origin: the Chinese have possessed the art from the commencement of the seventh century, and their ware is, in some respects, altogether unequalled. The materials employed by them are known to be *kaolin* or decomposed felspar; *petuntze*, or quartz reduced to fine powder; and the ashes of fern, which contain potassium carbonate.

Stoneware.—This is a coarse kind of porcelain, made from clay containing oxide of iron and a little lime, to which it owes its partial fusibility. The glazing is performed by throwing common salt into the heated furnace ; this is volatilised, and decomposed by the joint agency of the silica of the ware and of the vapour of water always present; hydrochloric acid and soda are produced, the latter forming a silicate, which fuses over the surface of the ware, and gives a thin, but excellent glaze.

Earthenware.—The finest kind of earthenware is made from a white secondary clay, mixed with a considerable quantity of silica. The articles are thoroughly dried and fired; after which they are dipped into a readily fusible glaze mixture, of which lead oxide is usually an important ingredient, and, when dry, reheated to the point of fusion of the latter. The whole process is much easier of execution than the making of porcelain, and demands less care. The ornamental designs in blue and other colours, so common upon plates and household articles, are printed upon paper in enamel pigment mixed with oil, and transferred, while still wet, to the unglazed ware. When the ink becomes dry, the paper is washed off, and the glazing completed.

The coarser kinds of earthenware are sometimes covered with a whitish opaque glaze, which contains the oxides of lead and tin; such glaze is very liable to be attacked by acids, and is dangerous for culinary vessels.

Crucibles, when of good quality, are very valuable to the chemist. They are made of clay free from lime, mixed with sand or ground ware of the same description. The Hessian and Cornish crucibles are among the best. Sometimes a mixture of plumbago and clay is employed for the same purpose ; and powdered coke has been also used with the earth : such crucibles bear rapid changes of temperature with impunity.

DYAD METALS.—GROUP II.

MAGNESIUM.

Atomic weight, 24. Symbol, Mg.

THIS metal was formerly classed with the metals of the alkaline earths, but it is much more nearly related to zinc by its properties in the free state, as well as by the volatility of its chloride, the solubility of its sulphate, and the isomorphism of several of its compounds with the analogously constituted compounds of zinc.

Magnesium occurs in the mineral kingdom as hydrate, carbonate, borate, phosphate, sulphate, and nitrate, sometimes in the solid state, sometimes dissolved in mineral waters: magnesian limestone, or dolomite, which forms entire mountain masses, is a carbonate of magnesium and calcium. Magnesium also occurs as silicate, com-

the reduction is
common clay tobacco-pipe over an Argand s
the negative pole being an iron wire passe
the positive pole a piece of gas-coke, just to
fused chlorides. On passing the current of
cells through the arrangement, the magne
extremity of the iron wire.

2. Magnesium may be prepared in mu
reducing magnesium chloride, or the double
and sodium or potassium, with metallic
chloride is prepared by dissolving magnesi
chloric acid, adding an equivalent quantity
chloride, evaporating to dryness, and fusing
duct, heated with sodium in a wrought-iron
magnesium, containing certain impurities,
freed by distillation. This process is now ca
facturing scale, and the magnesium is drawn
into riband for burning.*

Magnesium is a brilliant metal, almost as wh
more brittle at common temperatures, but ma
below redness. Its specific gravity is 1·74.
and volatilises at nearly the same temperature
lustre in dry air, but in moist air it becomes c
magnesia.

Magnesium in the form of wire or riband t
burning with a dazzling bluish-white light.
or spirit-lamp is sufficient to inflame it, but
combustion, the metal must be kept in contac
this purpose lamps are constructed, provide
which continually pushes three or more ma
small spirit-flame.

produced; but when this solution is evaporated to dryness, the last portions of water are retained with such obstinacy, that decomposition of the water is brought about by the concurring attractions of magnesium for oxygen, and of chlorine for hydrogen; hydrochloric acid is expelled, and magnesia remains. If, however, sal-ammoniac, potassium chloride, or sodium chloride is present, a double salt is produced, which is easily rendered anhydrous. The best mode of preparing the chloride is to divide a quantity of hydrochloric acid into two equal portions, to neutralise one with magnesia, and the other with ammonia, or carbonate of ammonia: to mix these solutions, evaporate them to dryness, and then expose the salt to a red heat in a loosely covered porcelain crucible. Sal-ammonaic sublimes, and magnesium chloride in a fused state remains; the latter is poured out upon a clean stone, and when cold transferred to a well-stopped bottle.

The chloride so obtained is white and crystalline. It is very deliquescent and highly soluble in water, from which it cannot again be recovered by evaporation, for the reasons just mentioned. When long exposed to the air in the melted state, it is converted into magnesia. It is soluble in alcohol.

Magnesium Oxide, or **Magnesia**, MgO.—This oxide is easily prepared by exposing the *magnesia alba* of pharmacy, which is a hydrocarbonate, to a full red heat in an earthen or platinum crucible. It forms a soft, white powder, which slowly attracts moisture and carbonic acid from the air, and unites quietly with water to a hydrate which possesses a feeble degree of solubility, requiring about 5000 parts of water at 15·5° and 36,000 parts at 100°. The alkalinity of magnesia can only be observed by placing a small portion in a moistened state upon test-paper: it neutralises acids, however, in the most complete manner. It is infusible.

Magnesium sulphide is formed by passing vapour of carbon sulphide over magnesia, in capsules of coke, at a strong red heat.

Oxysalts of Magnesium.—The *sulphate*, $MgSO_4.7H_2O$, commonly called Epsom salt, occurs in sea-water, and in many mineral springs, and is now manufactured in large quantities by acting on magnesian limestone with dilute sulphuric acid, and separating the magnesium sulphate from the greater part of the slightly soluble calcium sulphate by filtration. The crystals are derived from a right rhombic prism; they are soluble in an equal weight of water at 5·5°, and in a still smaller quantity at 100°. The salt has a nauseous bitter taste, and, like many other neutral salts, possesses purgative properties. When it is exposed to heat, 6 molecules of water readily pass off, the seventh being energetically retained. Magnesium sulphate forms beautiful double salts with the sulphates of potassium and ammonium, which contain 6 molecules of crystallisation-water, their formulæ being $MgK_2(SO_4)_2 6H_2O$, and $Mg(NH_4)_2(SO_4)_2 6H_2O$. These salts are isomorphous, and form monoclinic crystals.

Carbonates.—The *neutral carbonate*, $MgCO_3$ or $MgO.CO_2$, occurs native in rhombohedral crystals, resembling those of calc-spar, imbedded in talc-slate: a soft earthy variety is sometimes met with.

When magnesia alba is dissolved in aqueous carbonic acid, and the solution left to evaporate spontaneously, small prismatic crystals are deposited, consisting of trihydrated magnesium carbonate, $MgCO_3.3H_2O$.

The magnesia alba itself, although often called carbonate of magnesium, is not so in reality; it is a compound of carbonate with hydrate. It is prepared by mixing hot solutions of potassium or sodium carbonate and magnesium sulphate, the latter being kept in slight excess, boiling the whole a few minutes, during which time much carbonic acid is disengaged, and well washing the precipitate so produced. If the solution is very dilute, the magnesia alba is exceedingly light and bulky; if otherwise, it is denser. The composition of this precipitate is not perfectly constant. In most cases it contains $4MgCO_3.MgH_2O_2.6$ aq.

Magnesia alba is slightly soluble in water, especially when cold.

Magnesium phosphate, $MgHPO_4.7H_2O$, separates in small colourless prismatic crystals when solutions of sodium phosphate and magnesium sulphate are mixed and suffered to stand for some time. According to Graham, it is soluble in about 1000 parts of cold water. Magnesium phosphate exists in the grain of the cereals, and can be detected in considerable quantity in beer.

Magnesium and Ammonium Phosphate, $Mg(NH_4)PO_4.6H_2O$.—When ammonia or its carbonate is mixed with a magnesium salt, and a soluble phosphate is added, a crystalline precipitate having the above composition, subsides, immediately if the solutions are concentrated, and after some time if very dilute: in the latter case, the precipitation is promoted by stirring. This salt is slightly soluble in pure water, but nearly insoluble in saline and ammoniacal liquids. When heated, it gives off water and ammonia, and is converted into *magnesium pyrophosphate*, $Mg_2P_2O_7$:

$$2Mg(NH_4)PO_4 = Mg_2P_2O_7 + H_2O + 2NH_3 .$$

At a strong red heat it fuses to a white enamel-like mass. Magnesium and ammonium phosphate sometimes forms a urinary calculus, and occurs also in guano.

In analysis, magnesium is often separated from solutions by bringing it into this state. The liquid, free from alumina, lime, &c., is mixed with sodium phosphate and excess of ammonia, and gently heated for a short time. The precipitate is collected upon a filter and thoroughly washed with water containing a little ammonia, after which it is dried, ignited to redness, and weighed. The proportion of magnesia is then easily calculated.

Silicates.—The following natural compounds belong to this class: *Chrysolite*, $Mg_2SiO_4 = 2MgO.SiO_2$, a crystallised mineral, sometimes employed for ornamental purposes: a portion of the magnesia is commonly replaced by ferrous oxide, which communicates a green colour. *Meerschaum*, $2MgSiO_3.SiO_2=2MgO.3SiO_2$, is a soft sectile mineral, from which pipe-bowls are made. *Talc*, $4MgSiO_3.SiO_2.4$ aq. (called *steatite* when massive), is a soft, white, sectile, transparent or translucent mineral, used as firestones for furnaces and stoves, and in thin plates for glazing lanthorns, &c.; also in the state of powder for diminishing friction. *Soapstone*, also called steatite, is a silicate of magnesium and aluminium of somewhat variable composition. *Serpentine* is a combination of silicate and hydrate of magnesium. *Jade*, an exceedingly hard stone, brought from New Zealand, is a silicate of magnesium and aluminium: its green colour is due to chromium. *Augite* and *hornblende* are essentially double silicates of magnesia and lime, in which the magnesia is more or less replaced by its isomorphous substitute, ferrous oxide.

Magnesium salts are isomosphous with zinc salts, ferrous salts, cupric salts, cobalt salts, and nickel salts, &c.; they are usually colourless, and are easily recognised by the following characters:— A gelatinous white precipitate with *caustic alkalis*, including *ammonia*, insoluble in excess, but soluble in solution of sal-ammoniac. A white precipitate with *potassium* and *sodium carbonates*, but none with ammonium carbonate in the cold. A white crystalline precipitate with soluble *phosphates*, on the addition of a little ammonia.

ZINC.

Atomic weight, 65·2. Symbol, Zn.

ZINC is a somewhat abundant metal: it is found in the state of carbonate, silicate, and sulphide, associated with lead ores in many districts, both in Britain and on the Continent; large supplies are obtained from Silesia, and from the neighbourhood of Aachen. The native carbonate, or *calamine*, is the most valuable of the zinc ores, and is preferred for the extraction of the metal: it is first roasted to expel water and carbonic acid, then mixed with fragments of coke or charcoal, and distilled at a full red heat in a large earthen retort; carbon monoxide escapes, while the reduced metal volatilises and is condensed by suitable means, generally with minute quantities of arsenic.

Zinc is a bluish-white metal, which slowly tarnishes in the air: it has a lamellar, crystalline structure, a density varying from 6·8 to 7·2, and is, under ordinary circumstances, brittle. Between 120° and 150° it is, on the contrary, malleable, and may be rolled or hammered without danger of fracture; and, what is very remarkable, after such treatment, it retains its malleability when cold; the sheet-zinc of commerce is thus made. At 210° it is so brittle that it may be reduced to powder. At 412° it melts; at a bright red heat it boils and volatilises, and, if air be admitted, burns with a splendid greenish light, generating the oxide. Dilute acids dissolve zinc very readily: it is constantly employed in this manner for preparing hydrogen gas.

the former o
zinc in hydrochloric acid, and then addin
of sal-ammoniac, is very useful in tinning
and iron.

The *oxide*, ZnO, is a strong base, formin
the magnesium salts. It is prepared eit
atmospheric air, or by heating the carbona
is a white, tasteless powder, insoluble in w
by acids. When heated it is yellow, bu
cooling. It is getting into use as a substi
prepare zinc-white on a large scale, metal
large earthen muffles, whence the zinc va
receiver (*guérite*), where it comes in conta
and is oxidised. The zinc oxide thus for
into a condensing chamber divided into s
cloths suspended within it.

The *sulphate*, $ZnSO_4.7H_2O$, commonly
This salt is hardly to be distinguished by
sulphate: it is prepared either by dissolv
sulphuric acid, or, more economically, b
sulphide, or *blende*, which, by absorption of
part converted into sulphate. The altered
into water, and the salt obtained by evapor
Zinc sulphate has an astringent metallic
medicine as an emetic. The crystals diss
and in a much smaller quantity of hot wat
6 molecules of water have been observed. Zi
salts with the sulphates of potassium an
$ZnK_2(SO_4)_2.6H_2O$ and $Zn(NH_4)_2(SO_4)_2.6H_2O$
corresponding magnesium salts.

The *carbonate*, $ZnCO_3$, is found native

Zinc salts are distinguished by the following characters:—*Caustic potash*, *soda* and *ammonia*, give a white precipitate of hydrate, freely soluble in excess of the alkali. *Potassium* and *sodium carbonates* give white precipitates, insoluble in excess. *Ammonium carbonate* gives also a white precipitate, which is redissolved by an excess. *Potassium ferrocyanide* gives a white precipitate. *Hydrogen sulphide* causes no change in zinc solutions containing free mineral acids; but in neutral solutions, or with zinc salts of organic acids, such as the acetate, a white precipitate is formed. *Ammonium sulphide* throws down white sulphide of zinc, insoluble in caustic alkalis. The formation of this precipitate in a solution containing excess of caustic alkali, serves to distinguish zinc from all other metals.

All zinc compounds, heated on charcoal with sodium carbonate in the inner blowpipe flame, give an incrustation of zinc oxide, which is yellow while hot, but becomes white in cooling. If this incrustation be moistened with a dilute solution of cobalt nitrate, and strongly heated in the outer flame, a fine green colour is produced.

The applications of metallic zinc to the purposes of roofing, the construction of water channels, &c., are well known; it is sufficiently durable, but inferior in this respect to copper. It is much used also for protecting iron and copper from oxidation when immersed in saline solutions, such as sea-water, or exposed to damp air. This it does by forming an electric circuit, in which it acts as the positive or more oxidable metal (p. 287). *Galvanised iron* consists of iron having its surface coated with zinc.

CADMIUM.

Atomic weight, 112. Symbol, Cd.

THIS metal was discovered in 1817 by Stromeyer, and by Hermann: it accompanies the ores of zinc, especially those occurring in Silesia, and, being more volatile than that substance, rises first in vapour when the calamine is subjected to distillation with charcoal. Cadmium resembles tin in colour, but is somewhat harder; it is very malleable, has a density of 8·7, melts below 260°, and is nearly as volatile as mercury. It tarnishes but little in the air, but burns when strongly heated. Dilute sulphuric and hydrochloric acids act but little on cadmium in the cold; nitric acid is its best solvent.

The observed vapour-density of cadmium is 3·94 compared with air, or 56·3 compared with hydrogen, which latter number does not differ greatly from the half of 112, the atomic weight of the metal: hence it appears that the *atom* of cadmium in the state of vapour occupies twice the space of an atom of hydrogen (p. 250).

Cadmium, like zinc, is dyadic, and forms but one series of compounds. The *oxide*, CdO, may be prepared by igniting either the carbonate or the nitrate: in the former case it has a pale-brown colour, and in the latter a much darker tint, and forms octohedral microscopic crystals. Cadmium oxide is infusible: it dissolves in acids, producing a series of colourless salts: it attracts carbonic acid from the air, and turns white. The *sulphate*, $CdSO_4.4H_2O$, is easily obtained by dissolving the oxide or carbonate in dilute sulphuric acid: it is very soluble in water, and forms double salts with the sulphates of potassium and ammonium, which contain respectively $CdK_2(SO_4)_2.6H_2O$ and $Cd(NH_4)_2(SO_4)_2.6H_2O$ The *chloride*, $CdCl_2$, is a very soluble salt, crystallising in small four-sided prisms. The *sulphide*, CdS, is a very characteristic compound, of a bright yellow colour, forming microscopic crystals, fusible at a high temperature. It is obtained by passing sulphuretted hydrogen gas through a solution of the sulphate, nitrate, or chloride. This compound is used as a yellow pigment, of great beauty and permanence. It occurs native as *greenockite*.

Fixed caustic *alkalis* give with cadmium salts a white precipitate of hydrated oxide, insoluble in excess. *Ammonia* gives a similar white precipitate, readily soluble in excess. The *fixed alkaline carbonates*, and *ammonia carbonate*, throw down white cadmium carbonate, insoluble in excess of either precipitant. *Hydrogen sulphide* and *ammonium sulphide* precipitate the yellow sulphide of cadmium.

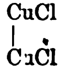
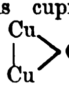
GROUP III.

COPPER.

Atomic weight, 63·4. Symbol, Cu (Cuprum).

COPPER is a metal of great value in the arts: it sometimes occurs in the metallic state, crystallised in octohedrons, or more frequently in dodecahedrons, but is more abundant in the form of red oxide, and in that of sulphide combined with sulphide of iron, as *yellow copper ore* or *copper pyrites*. Large quantities of the latter substance are annually obtained from the Cornish mines, and taken to South Wales for reduction, which is effected by a somewhat complex process. The principle of this may, however, be easily made intelligible. The ore is roasted in a reverberatory furnace, by which much of the iron sulphide is converted into oxide, while the copper sulphide remains unaltered. The product of this operation is then strongly heated with silicious sand; the latter combines with the iron oxide to a fusible *slag*, and separates from the heavier copper compound. When the iron has, by a repetition of these processes, been got rid of, the copper sulphide begins to decompose in the flame-furnace, losing its sulphur and absorbing oxygen; the temperature is then raised sufficiently to reduce the oxide thus produced, by the aid of carbonaceous matter. The last part of the operation consists in thrusting into the melted metal a pole of birch-wood, the object of which is probably to reduce a little remaining oxide by the combustible gases thus generated. Large quantities of extremely valuable ore, chiefly carbonate and red oxide, have lately been obtained from South Australia and Chile.

Copper has a well-known yellowish-red colour, a specific gravity of 8·96, and is very malleable and ductile : it is an excellent conductor of heat and electricity : it melts at a bright red heat, and seems to be slightly volatile at a very high temperature. Copper undergoes no change in dry air : exposed to a moist atmosphere, it becomes covered with a strongly adherent green crust, consisting in a great measure of carbonate. Heated to redness in the air, it is quickly oxidised, becoming covered with a black scale. Dilute sulphuric and hydrochloric acids scarcely act upon copper ; boiling oil of vitriol attacks it, with evolution of sulphurous oxide ; nitric acid, even dilute, dissolves it readily, with evolution of nitrogen dioxide.

Copper, in its most stable compounds, the cupric compounds, is bivalent, these compounds containing 1 atom of the metal combined with 2 atoms of a univalent, or 1 atom of a bivalent negative radicle, *e.g.*, $CuCl_2$, CuO, $Cu(NO_3)_2$, $CuSO_4$, &c. It also forms another series, the cuprous compounds, in which it may be regarded as univalent, *e.g.*, $CuCl$, Cu_2O, &c., like silver in the argentic compounds. On the other hand, the cuprous compounds may be supposed to be formed by addition of copper to the cupric compounds, the metal still remaining bivalent, thus cuprous chloride, $Cu_2Cl_2 =$  $\begin{array}{c}CuCl\\ |\\ CuCl\end{array}$; cuprous oxide, $Cu_2O =$  $\begin{array}{l}Cu\\ |\\ Cu\end{array}\!\!>O$. These compounds are very unstable, being easily converted into cupric compounds by the action of oxidising agents.

Copper Chlorides.—*Cupric chloride*, $CuCl_2$, is most easily prepared by dissolving cupric oxide in hydrochloric acid, and concentrating the green solution thence resulting. It forms green crystals, $CuCl_2 . 2H_2O$, very soluble in water and in alcohol : it colours the flame of the latter green. When gently heated, it parts with its water of crystallisation and becomes yellowish-brown ; at a high temperature it loses half its chlorine, and becomes converted into *cuprous chloride*. The latter is a white fusible substance, but little soluble in water, and prone to oxidation : it is formed when copper-filings or copper-leaf are put into chlorine gas ; also by precipitating a solution of cupric chloride or other cupric salt with stannous chloride :

$$2CuCl_2 + SnCl_2 = Cu_2Cl_2 + SnCl_4.$$

A plate of copper immersed in hydrochloric acid in a vessel containing air, becomes covered with white tetrahedrons of cuprous chloride. This compound dissolves in hydrochloric acid, forming a colourless solution, which gradually turns blue on exposure to the air.

A *hydrated cupric oxychloride*, $CuCl_2.3CuH_2O_2$, occurs native as *atacamite*.

Both the chlorides of copper form double salts with the chlorides of the alkali-metals.

Cuprous Hydride, Cu_2H_2.—When a solution of cupric sulphate is heated to about 70°, with hypophosphorous acid, this compound is deposited as a yellow precipitate, which soon turns red-brown. It gives off hydrogen when heated, takes fire in chlorine gas, and is converted by hydrochloric acid into cuprous chloride, with evolution of a double quantity of hydrogen, the acid giving up its hydrogen as well as the copper hydride :

$$Cu_2H_2 + 2HCl = Cu_2Cl_2 + 2H_2.$$

This reaction affords a remarkable instance of the union of two atoms of the same element to form a molecule (see page 259).

Copper Oxides.—Two oxides of copper are known, corresponding with the chlorides ; and a very unstable dioxide or peroxide, CuO_2, is said to be formed, as a yellowish brown powder, by the action of hydrogen dioxide on cupric hydrate.

Copper Monoxide, Cupric Oxide, or *Black Oxide of Copper,* CuO, is prepared by calcining metallic copper at a red heat, with full exposure to air, or, more conveniently, by heating the nitrate to redness, which then suffers complete decomposition. Cupric salts mixed with caustic alkali in excess, yield a bulky pale blue precipitate of hydrated cupric oxide, or cupric hydrate, CuH_2O_2 or $CuO.H_2O$, which, when the whole is raised to the boiling point, becomes converted into a heavy dark-brown powder: this also is anhydrous oxide of copper, the hydrate suffering decomposition, even in contact with water. The oxide prepared at a high temperature is perfectly black and very dense. Cupric oxide is soluble in acids, and forms a series of very important salts, isomorphous with magnesium salts.

Cuprous Oxide, Cu_2O, also called *Red Oxide* and *Suboxide of Copper.*—This oxide may be obtained by heating in a covered crucible a mixture of 5 parts of black oxide and 4 parts of fine copper filings ; or by adding grape sugar to a solution of cupric sulphate, and then putting in an excess of caustic potash ; the blue solution, heated to ebullition, is reduced by the sugar, and deposits cuprous oxide. This oxide often occurs in beautiful transparent ruby-red crystals, associated with other ores of copper, and can be obtained in the same state by artificial means. It communicates to glass a magnificent red tint, while that given by cupric oxide is green.

Cuprous oxide dissolves in excess of hydrochloric acid, forming a solution of cuprous chloride, from which that compound is precipitated on dilution with water. Most oxygen acids, namely, sulphuric, phosphoric, acetic, oxalic, tartaric, and citric acids, decompose cuprous oxide, forming cupric salts, and separating metallic copper; nitric acid converts it into cupric nitrate. Hence there are but few cuprous oxygen-salts, none indeed excepting the sulphites, and certain double sulphites formed by mixing a cupric solution with the sulphite of an alkali-metal, *e.g.*, ammonio-cuprous sulphite $Cu(NH_4)SO_3$ or $Cu_2(NH_4)_2(SO_3)_2$.

Cupric Oxysalts.—The *sulphate*, $CuSO_4.5H_2O$, commonly called *blue vitriol*, is prepared by dissolving cupric oxide in sulphuric acid or, at less expense, by oxidising the sulphide. It forms large blue triclinic prisms, soluble in four parts of cold and two parts of boiling water; when heated to 100° it readily loses four molecules of crystallisation-water, but the fifth is retained with great pertinacity, and is expelled only at a low red heat. At a very high temperature, cupric sulphate is entirely converted into cupric oxide, with evolution of sulphurous oxide and oxygen. Cupric sulphate combines with the sulphates of potassium and of ammonium, forming pale-blue salts, $CuK_2(SO_4)_2.6H_2O$ and $Cu(NH_4)_2(SO_4)_2.6H_2O$, isomorphous with the corresponding magnesium salts.

Cupric Nitrate, $Cu(NO_3)_2.3H_2O$, is easily made by dissolving the metal in nitric acid; it forms deep blue crystals, very soluble and deliquescent. It is highly corrosive. An insoluble basic nitrate is known; it is green.

Cupric Carbonates.—When sodium carbonate is added in excess to a solution of cupric sulphate, the precipitate is at first pale-blue and flocculent, but by warming it becomes sandy, and assumes a green tint; in this state it contains $CuCO_3.CuH_2O_2+aq$. This substance is prepared as a pigment. The beautiful mineral *malachite* has a similar composition, but contains no water of crystallisation, its composition being $CuCO_3.CuH_2O_2$. Another natural compound, called *azurite*, not yet artificially imitated, occurs in large transparent crystals of the most intense blue: it contains $2CuCO_3.CuH_2O_2$. *Verditer*, made by decomposing cupric nitrate with chalk, is said however, to have a somewhat similar composition.

Cupric Arsenite is a bright green insoluble powder, prepared by mixing the solutions of a cupric salt with an alkaline arsenite.

COPPER SULPHIDES.—There are two well-defined copper sulphides, analogous in composition to the oxides, and four others, containing larger proportions of sulphur, but of less defined constitution; these latter are precipitated from solutions of cupric salts by potassium pentasulphide.

Cupric Sulphide, CuS, occurs native as *indigo copper* or *covellin*, in soft bluish-black hexagonal plates and spheroïdal masses, and is produced artificially by precipitating cupric salts with hydrogen sulphide.

Cuprous Sulphide, Cu_2S, occurs native as *copper-glance* or *redruthite*, in lead-grey hexagonal prisms, belonging to the rhombic system; it is produced artificially by the combustion of copper-foil in sulphur vapour, by igniting cupric oxide with sulphur, and by other methods. It is a powerful sulphur-base, uniting with the sulphides of antimony, arsenic, and bismuth, to form several natural minerals. The several varieties of fahl-ore, or tetrahedrite, consist of cuprous sulphantimonite or sulpharsenite, in which the copper is more or less replaced by equivalent quantities of iron, zinc, silver, and mercury. The important ore, called *copper-pyrites*, is a cuproso-ferric sulphide, $Cu'Fe'''S_2$ or $Cu_2S.Fe_2S_3$, occurring in tetrahedral crystals of the quadratic system, or in irregular masses. Another species of copper and iron sulphide, containing various proportions of the two metals, occurs native, as *purple copper* or *erubescite*, in cubes, octohedrons, and other monometric forms.

Ammoniacal Copper-compounds.—The chlorides, sulphate, nitrate, and other salts of copper, unite with one or more molecules of ammonia, forming, for the most part, crystalline compounds of blue or green colour, some of which may be regarded as salts of metallammoniums (p. 363). Thus cupric chloride forms with ammonia, the compounds, $2NH_3.CuCl_2$, $4NH_3.CuCl_2$, and $6NH_3.CuCl_2$, the first of which may be formulated as *cupro-diammonium chloride*, $(N_2H_6Cu'')Cl_2$. Cupric sulphate forms, in like manner, *cupro-diammonium sulphate*, $(N_2H_6Cu'')SO_4$, which is a deep blue crystalline salt. Cuprous iodide forms with ammonia the compound, $4NH_3.Cu_2I_2$.

Caustic *potash* gives with cupric salts a pale blue precipitate of cupric hydrate, changing to blackish-brown anhydrous oxide on boiling.—*Ammonia* also throws down the hydrate; but, when in excess, redissolves it, yielding a deep purplish-blue solution.—*Potassium* and *sodium carbonates* give pale blue precipitates of cupric carbonate, insoluble in excess.—*Ammonium carbonate* the same, but soluble with deep blue colour.—*Potassium ferrocyanide* gives a fine red-brown precipitate of cupric ferrocyanide.—*Hydrogen sulphide* and *ammonium sulphide* afford black cupric sulphide, insoluble in ammonium sulphide.

The alloys of copper are of great importance. *Brass* consists of copper alloyed with from 28 to 34 per cent. of zinc; the latter may be added directly to the melted copper, or granulated copper may be heated with calamine and charcoal-powder, as in the old process. *Gun-metal*, a most valuable alloy, consists of 90 parts copper and 10 tin. *Bell* and *speculum metal* contain a still larger proportion of tin; these are brittle, especially the last named. A good bronze for statues is made of 91 parts copper, 2 parts tin, 6 parts zinc, and 1 part lead. The *brass* or *bronze* of the ancients is an alloy of copper with tin, often also containing lead, and sometimes zinc.

MERCURY.

Atomic weight, 200. Symbol, Hg (Hydrargyrum).

This very remarkable metal, sometimes called *quicksilver*, has been known from early times, and perhaps more than all others has excited the attention and curiosity of experimenters, by reason of its peculiar physical properties. Mercury is of great importance in several of the arts, and enters into the composition of many valuable medicaments.

Metallic mercury is occasionally met with in globules disseminated through the native sulphide, which is the ordinary ore. This latter substance, sometimes called *cinnabar*, is found in considerable quantity in several localities, of which the most celebrated are Almaden in Spain, and Idria in Austria. Only recently it has been discovered in great abundance, and of remarkable purity, in California and Australia. The metal is obtained by heating the sulphide in an iron retort with lime or scraps of iron, or by roasting it in a furnace, and conducting the vapours into a large chamber, where the mercury is condensed, while the sulphurous acid is allowed to escape. Mercury is imported into this country in bottles of hammered iron, containing seventy-five pounds each, and in a state of considerable purity. When purchased in smaller quantities, it is sometimes found adulterated with tin and lead, which metals it dissolves to some extent without much loss of fluidity. Such admixture may be known by the foul surface the mercury exhibits when shaken in a bottle containing air, and by the globules, when made to roll upon the table, leaving a train or tail.

Mercury has a nearly silver-white colour, and a very high degree of lustre : it is liquid at all ordinary temperatures, and solidifies only when cooled to – 40°. In this state it is soft and malleable. At 350° it boils, and yields a transparent, colourless vapour, of great density. The metal volatilises, however, to a sensible extent at all temperatures above 19° or 21°; below this point its volatility is imperceptible. The volatility of mercury at the boiling heat is much retarded by the presence of minute quantities of lead or zinc. The specific gravity of mercury at 15·5° is 13·59 ; that of frozen mercury about 14, great contraction taking place in the act of solidification.

Pure mercury is quite unalterable in the air at common temperatures, but when heated to near its boiling point, it slowly absorbs oxygen, and becomes converted into a crystalline dark-red powder, which is the highest oxide. At a dull red heat this oxide is again decomposed into its constituents. Hydrochloric acid has little or no action on mercury, and the same may be said of sulphuric acid in a diluted state : when the latter is concentrated and boiling hot, it oxidises the metal, converting it into mercuric sulphate, with evolution of sulphurous oxide. Nitric acid, even dilute and in the cold dissolves mercury freely, with evolution of nitrogen dioxide.

The observed vapour-density of mercury referred to air as unity is 6·7 ; this referred to hydrogen is nearly 100 ;* that is to say, half the atomic weight of the metal : consequently the atom of mercury, like that of cadmium, occupies in the gaseous state twice the volume of an atom of hydrogen (see page 251).

Mercury forms two series of compounds, namely, the mercuric compounds, in which it is bivalent, as $HgCl_2$, HgO, $HgSO_4$, &c., and the mercurous compounds, in which it is apparently univalent, as Hg_2Cl_2, Hg_2O, &c. These compounds are analogous in constitution to the cupric and cuprous compounds ; and the mercurous compounds, like the latter, are easily converted into mercuric compounds by the action of oxidising agents, which remove one atom of mercury ; but they are, on the whole, much more stable than the cuprous compounds.

Mercury Chlorides.—*Mercuric chloride*, $HgCl_2$, commonly called *Corrosive Sublimate*.—This compound may be obtained by several different processes: (1.) When metallic mercury is heated in chlorine gas, it takes fire and burns, producing this substance. (2.) It may be made by dissolving mercuric oxide in hot hydrochloric acid, crystals of corrosive sublimate then separating on cooling. (3.) Or, more economically, by subliming a mixture of equal parts of mercuric sulphate and dry common salt ; and this is the plan generally followed. The decomposition is represented by the equation :

$$HgSO_4 + 2NaCl = HgCl_2 + Na_2SO_4 .$$

Sublimed mercuric chloride forms a white transparent crystalline mass, of specific gravity 5·43 ; it melts at 265°, boils at 295°, and volatilises somewhat more easily than calomel, even at ordinary temperatures. Its observed vapour-density, referred to hydrogen as unity, is 140 : and the density calculated from the formula $HgCl_2$, supposing that the molecule occupies the same space as a molecule or two atoms of hydrogen, p. 251 is $\frac{200 + 2 . 35{\cdot}5}{2} = 135{\cdot}5$; the near agreement of this number with the observed result shows that the vapour is in the normal state of condensation.

Mercuric chloride dissolves in 16 parts of cold and 3 parts of boiling water, and crystallises from a hot solution in long white prisms. Alcohol and ether also dissolve it with facility ; the latter even withdraws it from a watery solution.

Mercuric chloride combines with a great number of other metallic chlorides, forming a series of beautiful double salts, of which the ancient *sal alembroth* may be taken as a good example : it contains $HgCl_2.2NH_4Cl.H_2O$. Corrosive sublimate absorbs ammoniacal gas with great avidity, generating the compound $HgCl_2.NH_3$.

Mercuric chloride forms several compounds with mercuric oxide. These are produced by several processes, as when an alkaline carbonate is added in varying proportions to a solution of mercuric chloride. They differ greatly in colour and physical character, and are mostly decomposed by water.

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* $\frac{6{\cdot}7}{0{\cdot}6926} = 98{\cdot}3$.

Mercuric chloride forms insoluble compounds with many of the azotised organic principles, as albumin, &c. It is perhaps to this property that its strong antiseptic properties are due. Animal and vegetable substances are preserved by it from decay, as in Kyan's method of preserving timber and cordage. Albumin is on this account an excellent antidote to corrosive sublimate in cases of poisoning.

Mercurous Chloride, Hg_2Cl_2, commonly called *Calomel.*—This very important substance may be easily and well prepared by pouring a solution of mercurous nitrate into a large excess of dilute solution of common salt. It falls as a dense white precipitate, quite insoluble in water; it must be thoroughly washed with boiling distilled water, and dried. Calomel is, however, generally procured by another and more complex process. Dry mercuric sulphate is rubbed in a mortar with as much metallic mercury as it already contains, and a quantity of common salt, until the globules disappear, and an uniform mixture has been produced. This is subjected to sublimation, and the vapour of the calomel being carried into an atmosphere of steam, or into a chamber containing air, is thus condensed in a minutely divided state, and the laborious process of pulverisation of the sublimed mass is avoided. The reaction is thus explained:

$$HgSO_4 + Hg + 2NaCl = Hg_2Cl_2 + Na_2SO_4.$$

Pure calomel is a heavy, white, insoluble tasteless powder: it rises in vapour at a temperature below redness, and is obtained by ordinary sublimation as a yellowish white crystalline mass. It is as insoluble in cold dilute nitric acid as silver chloride; boiling-hot strong nitric acid oxidises and dissolves it. Calomel is instantly decomposed by an alkali, or by lime-water, with production of mercurous oxide. It is sometimes apt to contain a little mercuric chloride, which would be a very dangerous contamination in calomel employed for medical purposes. This is easily discovered by boiling with water, filtering the liquid, and adding caustic potash. Any corrosive sublimate is indicated by a yellow precipitate.

The observed vapour-density of calomel referred to hydrogen as unity, is 119·2. Now the formula Hg_2Cl_2, if it represents a molecule occupying in the gaseous state two volumes (*i.e.*, twice the volume of an atom of hydrogen, p. 251), would give a density nearly double of this: for $\frac{400 + 2\,.\,35{\cdot}5}{2} = 235{\cdot}5$. Hence it might be inferred that the composition of calomel should rather be represented by the simpler formula HgCl, which would give for the vapour-density the number 117·75. The frequent decomposition of mercurous salts into mercuric salts and free mercury is however in favour of the supposition that their molecules contain two atoms of mercury; and the anomaly in the vapour-volume of calomel may be explained by supposing that the vapour of this compound, like that of many

mixed with merc
which is at first yellow, but in a few
brilliant scarlet, this colour being reta
neutral iodide: it may be made, altho
triturating equivalent quantities of iodi
alcohol. In preparing it by precipitati
the proper proportions of the two salts,
excess of either, more especially in
Mercuric iodide exhibits a very rema
attended with difference of colour, whicl
to the figure assumed. Thus, when the
to a high temperature, it becomes brig
yields a copious sublimate of minute b
If in this state it be touched by a hard
red, and the same change happens spo
lapse of time. On the other hand, by
heating, a sublimate of red crystals, havi
may be obtained, which are permanent.
happens with the freshly precipitated i
first formed breaking up in a few seconds,
to the red modification.

Mercuric iodide forms double salts with
metallic iodides, as those of the alkali-m
metals; thus it dissolves in aqueous pota
solution deposits, on cooling, crystals of
$2(KI.HgI_2).3H_2O$. They are decomposed
of about half the mercuric iodide, the sol
salt, $2KI.HgI_2$, which remains as a saline

Mercurous Iodide, Hg_2I_2, is formed whe
iodide is added to mercurous nitrate: it
yellow, insoluble precipitate, with a ti
prepared b

cautiously heating any of the mercuric or mercurous nitrates to complete decomposition, whereby the acid is decomposed and expelled, oxidising the metal to a maximum, if it happens to be in the state of mercurous salt. The product thus obtained is also crystalline and very dense, but has a much paler colour than the preceding; while hot, it is nearly black. It is by this method that the oxide is generally prepared: it is apt to contain undecomposed nitrate, which may be discovered by strongly heating a portion in a test-tube: if red fumes are produced, or the odour of nitrous acid exhaled, the oxide has been insufficiently heated in the process of manufacture. (3.) By adding caustic potash in excess to a solution of corrosive sublimate, by which a bright yellow precipitate of mercuric oxide is thrown down, which differs from the foregoing preparations merely in being destitute of crystalline texture and much more minutely divided. It must be well washed and dried.

Mercuric oxide is slightly soluble in water, communicating to the latter an alkaline reaction and metallic taste: it is highly poisonous. When strongly heated, it is decomposed, as before observed, into metallic mercury and oxygen gas.

Mercurous Oxide, Hg_2O; *Suboxide*, or *Grey Oxide of Mercury.*—This oxide is easily prepared by adding caustic potash to mercurous nitrate, or by digesting calomel in solution of caustic alkali. It is a dark grey, nearly black, heavy powder, insoluble in water, slowly decomposed by the action of light into metallic mercury and red oxide. The preparations known in pharmacy by the names *blue pill*, *grey ointment*, *mercury with chalk*, &c., often supposed to owe their efficacy to this substance, merely contain the finely divided metal.

Mercury Nitrates.—Nitric acid varies in its action upon mercury, according to the temperature. When cold and somewhat diluted, it forms only mercurous salts, and these are neutral or basic—*i.e.*, oxynitrates (p. 324)—as the acid or the metal happens to be in excess. When, on the contrary, the nitric acid is concentrated and hot, the mercury is raised to its highest state of oxidation, and a mercuric salt is produced. Both classes of salts are apt to be decomposed by a large quantity of water, giving rise to insoluble, or sparingly soluble, basic compounds.

Mercuric Nitrates.—By dissolving mercuric oxide in excess of nitric acid, and evaporating gently, a syrupy liquid is obtained, which, enclosed in a bell-jar over lime or sulphuric acid, deposits bulky crystals and crystalline crusts, both having the composition $2Hg(NO_3)_2.H_2O$. The same substance is deposited from the syrupy liquid as a crystalline powder by dropping it into concentrated nitric acid. The syrupy liquid itself appears to be a definite compound, containing $Hg(NO_3)_2.H_2O$. By saturating hot dilute nitric acid with mercuric oxide, a salt is obtained on cooling, which crystallises in needles, permanent in the air, containing $Hg(NO_3)_2.HgO.H_2O$. The preceding crystallised salts are decomposed by water, with production of compounds more and more basic as the washing is prolonged, or the temperature of the water raised.

Mercurous Nitrate, $(Hg_2)(NO_3)_2.2H_2O$, forms large colourless crystals soluble in a small quantity of water without decomposition; it is made by dissolving mercury in an excess of cold dilute nitric acid.

When excess of mercury has been employed, a finely crystallised basic salt is deposited after some time, containing $(Hg_2)(NO_3)_2.2Hg_2O.3H_2O$, or $3Hg_2O.N_2O_5.3H_2O$; this is also decomposed by water. The two salts are easily distinguished when rubbed in a mortar with a little sodium chloride; the neutral compound gives sodium nitrate and calomel; the basic salt, sodium nitrate and a black compound of calomel with mercurous oxide. A black substance, called *Hahnemann's soluble mercury*, is produced when ammonia in small quantity is dropped into a solution of mercurous nitrate: it contains $2NH_3.3Hg_2O.N_2O_5$, or, according to Kane, $2NH_3.2Hg_2O.N_2O_5$; the composition of this preparation evidently varies according to the temperature and the concentration of the solutions.

Mercury Sulphates.—*Mercuric Sulphate*, $HgSO_4$, is readily prepared by boiling together oil of vitriol and metallic mercury until the latter is wholly converted into a heavy white crystalline powder, which is the salt in question; the excess of acid is then removed by evaporation carried to perfect dryness. Equal weights of acid and metal may be conveniently employed. Water decomposes the sulphate, dissolving out an acid salt, and leaving an insoluble, yellow, basic compound, formerly called *turpith* or *turbeth mineral*, containing, according to Kane's analysis, $HgSO_4.2HgO$, or $3HgO.SO_3$. Long-continued washing with hot water entirely removes the remaining acid, and leaves pure mercuric oxide.

Mercurous Sulphate, Hg_2SO_4, falls as a white crystalline powder when sulphuric acid is added to a solution of mercurous nitrate: it is but slightly soluble in water.

Mercury Sulphides.—*Mercuric Sulphide*, HgS, occurs native as cinnabar, a dull red mineral, which is the most important ore of mercury. Hydrogen sulphide passed in small quantity into a solution of mercuric nitrate, or chloride, forms a white precipitate, which is a compound of mercuric sulphide with the salt itself. An excess of the gas converts the whole into sulphide, the colour at the same time changing to black. When this black sulphide is sublimed, it becomes dark red and crystalline, but undergoes no change of composition: it is then *cinnabar* or *vermilion*. Mercuric sulphide is most easily prepared by subliming an intimate mixture of 6 parts of mercury and 1 part of sulphur, and reducing the resulting cinnabar to very fine powder, the beauty of the tint depending much upon the extent to which division is carried. The red or crystalline sulphide may also be formed directly, without sublimation, by heating the black precipitated substance in a solution of potassium pentasulphide; the mercuric sulphide is, in fact, soluble to a certain extent, in the alkaline sulphides, and forms with them crystallisable compounds.

When vermilion is heated in the air, it yields metallic mercury and sulphurous oxide: it resists the action both of caustic alkalis in solution, and of strong mineral acids, even nitric, and is attacked only by nitro-muriatic acid.

Mercurous sulphide, Hg_2S, is obtained by passing hydrogen sulphide into a solution of mercurous nitrate, as a black precipitate, which is resolved at a gentle heat into mercuric sulphide and metallic mercury.

Ammoniacal Mercury Compounds.— Mercurammonium Salts.—By the action of ammonia and its salts on mercury compounds, a variety of substances are formed which may be regarded as salts of mercurammoniums—that is, of ammonium-molecules in which the hydrogen is more or less replaced by mercury, in the proportion of 100 or 200 parts of mercury to 1 part of hydrogen, according as the compound is formed from a mercurous or a mercuric salt. The following are the most important of these compounds :—

Mercuric Compounds. — *Mercuro-diammonium chloride*, $(N_2H_6Hg'')Cl_2$, known in pharmacy as *fusible white precipitate*, is produced by adding potash to a solution of ammonio-mercuric chloride, $(2NH_4Cl.HgCl_2)$, or by dropping solution of mercuric chloride into a boiling solution of sal-ammoniac containing free ammonia, as long as the resulting precipitate redissolves: it then separates on cooling in regular dodecahedrons. At a gentle heat it gives off ammonia, leaving a chloride of mercurammonium and hydrogen, $(NH_2Hg'')Cl.HCl$:

$$N_2H_6Hg''Cl_2 = NH_3Hg''Cl_2 + NH_3.$$

Mercurammonium chloride, $(NH_2Hg'')Cl$.—This salt, known in pharmacy as *infusible white precipitate*, is formed by adding ammonia to a solution of mercuric chloride. When first produced, it is bulky and white, but by contact with hot water, or by much washing with cold water, it is converted into hydrated dimercurammouium chloride, $NHg''_2Cl.H_2O$.

Trimercuro-diammonium nitrate, $(N_2H_2Hg''_3)(NO_3)_2.2H_2O$, is formed as a white precipitate, on mixing a dilute and very acid solution of mercuric nitrate with very dilute ammonia.

Trimercuro-diamine, $N_2Hg''_3$, a compound derived from a double molecule of ammonia, N_2H_6, by substitution of 3 atoms of bivalent mercury for 6 atoms of hydrogen, is formed by passing dry ammonia gas over dry precipitated mercuric oxide :

$$3HgO + 2NH_3 = N_2Hg_3 + 3H_2O.$$

The excess of oxide being removed by nitric acid, the trimercurodiamine is obtained as a dark brown powder, which explodes by heat, friction, percussion, or contact with oil of vitriol, almost as violently as nitrogen chloride.

Dimercurammonium chloride, $NHg''_2Cl.H_2O$, is obtained, as already observed, by boiling mercurodiammonium chloride (infusible white precipitate), with water. It is a heavy, granular, yellow powder, which turns white again when treated with sal-ammoniac.

Dimercurammonium iodide, $NHg''_2I.H_2O$.—This compound may be formed by digesting the corresponding chloride in a solution of potassium iodide; or by heating mercuric iodide with excess of aqueous ammonia:

$$2HgI_2 + 4NH_3 + H_2O = NHg''_2I.H_2O + 3NH_4I;$$

also by passing ammonia gas over mercuric oxy-iodide:

$$Hg_4I_2O_3 + 2NH_3 = 2(NHg''_2I.H_2O) + H_2O;$$

and, lastly, by adding ammonia to a solution of potassio-mercuric iodide mixed with caustic potash:

$$2(2KI.HgI_2) + NH_3 + 3KHO = NHg''_2I.H_2O + 7KI + 2H_2O.$$

This last reaction affords an extremely delicate test for ammonia. A solution of potassio-mercuric iodide is prepared by adding potassium iodide to a solution of corrosive sublimate, till a portion only of the resulting red precipitate is redissolved, then filtering, and mixing the filtrate with caustic potash. The liquid thus obtained forms, with a very small quantity of ammonia, either free or in the form of an ammoniacal salt, a brown precipitate, soluble in excess of potassium iodide. This is called Nesler's test for ammonia.

Dimercurammonium Hydroxide, $NHg''_2(HO)$.—This compound is formed by treating precipitated mercuric oxide with aqueous ammonia, or by treating either of the dimercurammonium salts with a caustic alkali. It is a brown powder, which dissolves in acids, yielding salts of dimercurammonium.

Dimercurammonium Sulphate, $(NHg''_2)_2SO_4.2H_2O$, formerly called *ammoniacal turpethum*, is prepared by dissolving mercuric sulphate in ammonia, and precipitating the solution with water. It is a heavy white powder, yellowish when dry, resolved by heat into water, nitrogen, ammonia, and mercurous sulphate.

Mercurous Compounds. — *Mercurosammonium Chloride*, $NH_3Hg'Cl$, is the black precipitate formed when dry calomel is exposed to the action of ammonia gas. When exposed to the air, it gives off ammonia and leaves white mercurous chloride.—*Dimercurosammonium chloride*, $NH_2Hg'_2Cl$, is formed, together with sal-ammoniac, by digesting calomel in aqueous ammonia:

$$Hg_2Cl_2 + 2NH_3 = NH_2Hg_2Cl + NH_4Cl.$$

It is grey when dry, and is not altered by boiling water.—*Dimercurosammonium nitrate*, $2(NH_2Hg_2)NO_3.H_2O$. This, according to Kane, is the composition of the velvet-black precipitate known as Hahnemann's soluble mercury, which is produced on adding ammonia to a solution of mercurous nitrate. According to C. G. Mitscherlich, on the other hand, the precipitate thus formed has the composition $2NH_3.N_2O_5.3Hg_2O$, which is that of a hydrated *trimercurosammonium nitrate*, $2(NHHg_3)NO_3.2H_2O$.

Reactions of Mercury Salts.—All mercury compounds are volatilised or decomposed by a temperature of ignition: those which fail to yield the metal by simple heating may in all cases be made to do so by heating in a test-tube with a little dry sodium carbonate. The metal is precipitated from its soluble combinations by a plate of *copper*, and also by a solution of *stannous chloride* used in excess.

Hydrogen sulphide, and *Ammonium sulphide*, produce in solutions, both of mercuric and of mercurous salts, black precipitates insoluble in ammonium sulphide. In mercuric salts, however, if the quantity of the reagent added is not sufficient for complete decomposition, a white precipitate is formed, consisting of a compound of mercuric sulphide with the original salt, and often coloured yellow or brown by excess of mercuric sulphide. An excess of hydrogen sulphide, or ammonium sulphide, instantly turns the precipitate black. This reaction is quite characteristic of mercuric salts.

Mercuric salts are further distinguished by forming a yellow precipitate with caustic *potash* or *soda;* white with *ammonia* or *ammonium carbonate*, insoluble in excess ; red-brown with *potassium* or *sodium carbonate.* With *potassium iodide* they yield a bright scarlet precipitate, soluble in excess, either of the mercuric salt or of the alkaline iodide.

Mercurous salts are especially characterised by forming, with *hydrochloric acid* or *soluble chlorides*, a white precipitate which is turned black by ammonia. They also yield black precipitates with *caustic alkalis;* white with *alkaline carbonates*, soon turning black ; greenish-yellow with *potassium iodide.*

Alloys of mercury with other metals are termed *amalgams:* mercury dissolves in this manner many of the metals, as gold, silver, tin, lead, &c. These combinations sometimes take place with considerable violence, as in the case of potassium, in which light and heat are produced ; besides this, many of the amalgams after a while become solid and crystalline. The amalgam of tin used in silvering looking-glasses, and that of silver and of copper, sometimes employed for stopping hollow teeth, are examples. The solid amalgams appear to be, for the most part, definite compounds, while the liquid amalgams may be regarded, in many instances, as solutions of definite compounds in excess of mercury, inasmuch as, when they are pressed between chamois leather, mercury, containing only a small quantity of the other metal passes through, while a solid amalgam, frequently of definite atomic constitution, remains behind. A native compound of mercury and silver, called "amalgam" by mineralogists, and having the composition Ag_2Hg_2, or Ag_2Hg_3, is found crystallised in octohedrons, rhombic dodecahedrons, and other forms of the regular system.

CLASS III.—TRIAD METALS.

THALLIUM.

Atomic weight, 204. Symbol, Tl.

THIS element was discovered by Crookes, in 1861, in the seleniferous deposit of a lead-chamber of a sulphuric acid factory in the Hartz mountains, where iron pyrites is used for the manufacture of sulphuric acid. The name is derived from θαλλός, "green," because the existence of this metal was first recognised by an intense green line, appearing in the spectrum of a flame in which thallium is volatilised. It was at first suspected to be a metalloïd, but further examination proved it to be a true metal. It was first obtained in a distinct metallic form by Crookes towards the end of the year 1861, and soon afterwards by Lamy, who prepared it from the deposit in the lead-chamber of M. Kuhlmann, of Lille, where Belgian pyrites is employed for the manufacture of sulphuric acid.

Thallium appears to be very widely diffused as a constituent of iron and copper pyrites, though it never constitutes more than the 4000th part of the bulk of the ores. It has also been found in lepidolite from Moravia, in mica from Zinnwald in Bohemia, and in the mother-liquors of the salt-works at Nauheim.

Thallium is most economically prepared from the flue-dust of pyrites burners. This substance is stirred up in wooden tubs with boiling water, and the clear liquor, siphoned off from the deposit, is mixed with excess of strong hydrochloric acid, which precipitates impure thallium monochloride. To obtain a pure salt, this crude chloride is added by small portions at a time to half its weight of hot oil of vitriol in a porcelain or platinum dish, the mixture being constantly stirred, and the heat continued till the whole of the hydrochloric acid and the greater portion of the excess of sulphuric acid are driven off. The fused acid sulphate is now to be dissolved in an excess of water, and an abundant stream of hydrogen sulphide passed through the solution. The precipitate, which may contain arsenic, antimony, bismuth, lead, mercury, and silver, is separated by filtration, and the filtrate is boiled till all free hydrogen sulphide is removed. The liquid is now to be rendered alkaline with ammonia, and boiled; the precipitate of iron oxide and alumina, which generally appears in this place, is filtered off; and the clear solution evaporated to a small bulk. Thallium sulphate then separates on cooling, in long clear prismatic crystals.

Metallic thallium may be reduced from the solution of the sulphate, either by electrolysis, or by the action of zinc.

Thallium is a heavy metal, resembling lead in its physical properties. When freshly cut, it exhibits a brilliant metallic lustre and greyish colour, somewhat between those of silver and lead, assuming a slight yellowish tint by friction with harder bodies. It is very soft, being readily cut with a knife, and making a streak on paper like plumbago. It is very malleable, is not easily drawn into wire, but may be readily squeezed into that form by the process technically called "squirting." It has a highly crystalline structure and crackles like tin when bent. It melts at 294°.

In contact with the air, thallium tarnishes more rapidly than lead, becoming coated with a thin layer of oxide, which preserves the rest of the metal.

The most characteristic property of thallium is the bright green colour which the metal or any of its compounds impart to a colourless flame; and this colour, when viewed by the spectroscope, is seen to be absolutely monochromatic, appearing as one intensely brilliant and sharp green line.

Thallium dissolves in hydrochloric, sulphuric, and nitric acids, the latter attacking it very energetically, with copious evolution of red vapours.

Thallium forms two classes of compounds—namely, the thallious compounds, in which it is univalent: and the thallic compounds, in which it is trivalent. Thus it forms two oxides, Tl_2O and Tl_2O_3, with corresponding chlorides, bromides, iodides, and oxygen-salts. In some of its chemical relations it resembles the alkali-metals, forming a readily soluble and highly alkaline monoxide, a soluble and alkaline carbonate, an insoluble platinochloride, a thallio-aluminic sulphate, similar in form and composition to common potash-alum, and several phosphates exactly analogous in composition to the phosphates of sodium. In most respects, however, it is more nearly allied to the heavy metals, especially to lead, which it resembles closely in appearance, density, melting-point, specific heat, and electric conductivity.

Thallium Chlorides.—Thallium forms four chlorides, represented by the formulæ $TlCl$, Tl_4Cl_6, Tl_2Cl_4, and $TlCl_3$; the second and third of which may be regarded as compounds of the monochloride and trichloride.

The *Monochloride* or *Thallious Chloride*, $TlCl$, is formed by direct combination, the metal burning when heated in chlorine gas; or as a white curdy precipitate, resembling silver chloride, by treating the solution of any thallious salt with a soluble chloride. When boiled with water it dissolves like lead chloride, and separates in white crystals on cooling. It forms double salts with trichloride of gold and tetrachloride of platinum. The *platinum salt*, $2TlCl.PtCl_4$, separates as a pale yellow very slightly soluble crystalline powder, on adding platinic chloride to thallious chloride.

The *Trichloride* or *Thallic chloride*, $TlCl_3$, is obtained by dissolving the trioxide in hydrochloric acid, or by acting upon thallium, or one of the lower chlorides, with a large excess of chlorine at a gentle heat. It is soluble in water, and separates by evaporation in a vacuum in hydrated crystals; melts easily, and decomposes at a high temperature. It forms crystalline double salts with the chlorides of the alkali-metals.

The *Sesquichloride*, $Tl_4Cl_6 = TlCl_3.3TlCl$, is produced by dissolving thallium or the monochloride in nitromuriatic acid, and separates on cooling in yellow crystalline scales. By aqueous ammonia, potash, or even by thallious oxide, it is instantly decomposed into sesquioxide and monochloride, according to the equation:

$$2Tl_4Cl_6 + 3KHO = Tl_2O_3 + 6TlCl + 3KCl + 3HCl.$$

The *Dichloride*, $Tl_2Cl_4 = TlCl_3.TlCl$, is formed by carefully heating thallium or the monochloride, in a slow current of chlorine. It is a pale yellow substance reduced to sesquichloride by further heating.

The BROMIDES of thallium resemble the chlorides.

Iodides.—*Thallious Iodide*, TlI, is formed by direct combination of its elements, or by double decomposition. It forms a beautiful yellow powder, rather darker than sulphur, and melting, below redness, to a scarlet liquid, which, as the mass cools, remains scarlet for some time after solidification, then changes to bright yellow. The dried precipitate, when spread on paper with a little gum-water, undergoes a similar but opposite change to that experienced by mercuric iodide when heated, the yellow surface when held over a flame suddenly becoming scarlet, and frequently remaining so after cooling for several days; hard friction with a glass rod, however, changes the scarlet colour back to yellow. It is very slightly soluble in water, requiring, according to Crookes, 4453 parts of water at 17·2°, and 842·4 parts at 100°, to dissolve it.

Thallic Iodide, TlI_3, is formed by the action of thallium on iodine dissolved in ether, as a brown solution which gradually deposits rhombic prisms. It forms crystalline compounds with the iodides of the alkali-metals.

Thallium Oxides.—Thallium forms a monoxide and a trioxide.

The *Monoxide*, or *Thallious Oxide*, Tl_2O, constitutes the chief part of the crust which forms on the surface of the metal when exposed to the air. It may be prepared by allowing granulated thallium to oxidise in warm moist air, and then boiling with water. The filtered solution first deposits white needles of thallium carbonate, and, on further cooling, yellow needles of the hydroxide, TlHO or $Tl_2O.H_2O$, which, when left over oil of vitriol in a vacuum, yields the anhydrous monoxide as a reddish black mass retaining the shape of the crystals. It is partially reduced to metal by hydrogen at a red heat. When fused with sulphur it yields thallious sulphide. It dissolves readily in water, forming a colourless strongly alkaline solution, which reacts with metallic salts very much like caustic potash. This solution treated with zinc, or subjected to electrolysis, yields metallic thallium.

The *Trioxide*, or *Thallic Oxide*, is the chief product obtained by burning thallium in oxygen gas. It is best prepared by adding potash to the solution of a thallic salt, and drying the precipitate at 260°. It is also formed by electrolysis of thallious sulphate. It is a dark red powder reduced to thallious oxide at a red heat; neutral, insoluble in water and in alkalis. Thallic hydrate, $Tl'''HO_2$, is obtained by drying the above-mentioned precipitate at 100°.

Oxygen-salts.—Both the oxides of thallium dissolve readily in acids, forming crystalline salts, soluble in water; there are also a few insoluble thallium salts formed by double decomposition.

Thallious carbonate, Tl_2CO_3, is deposited in crystals, apparently trimetric, when a solution of thallious oxide is exposed to the air. It is soluble in water, and the solution has a slightly caustic taste and alkaline reaction.

Sulphates.—Thallious sulphate, Tl_2SO_4, obtained by evaporating the chloride or nitrate with sulphuric acid, or by heating metallic thallium with that acid, crystallises in anhydrous rhombic prisms, isomorphous with potassium sulphate. It forms, with aluminium sulphate, the salt, $AlTl(SO_4)_2.12H_2O$, isomorphous with common alum; and with the sulphates of magnesium, nickel, &c., double salts containing 6 molecules of water, and isomorphous with magnesium and potassium sulphate, &c. (p. 409).—*Thallic sulphate*, $Tl_2(SO_4)_3.7H_2O$, separates by evaporation from a solution of thallic oxide in dilute sulphuric acid, in thin colourless laminæ, which are decomposed by water, even in the cold, with separation of brown thallic oxide.

Phosphates.—The thallious phosphates form a series nearly as complete as those of the alkali-metals, which they also resemble in their behaviour when heated. There are three *orthophosphates*, containing respectively H_2TlPO_4, HTl_2PO_4, and Tl_3PO_4. The first two are soluble in water; the second is obtained by neutralising dilute phosphoric acid at boiling heat with thallious carbonate, and the first by mixing the dithallious salt with excess of phosphoric acid. The *trithallious salt*, Tl_3PO_4, is very sparingly soluble, and is formed as a crystalline precipitate on mixing the saturated solutions of ordinary disodic phosphate and thallious sulphate; also, together with ammonio-thallious phosphate, by treating the monothallious or dithallious salt with excess of ammonia. There are two *thallious pyrophosphates*, $H_2Tl_2P_2O_7$, and $Tl_4P_2O_7$, both very soluble in water: the first produced by carefully heating monothallious orthophosphate, the second by strongly heating dithallious orthophosphate. Of *thallious metaphosphate*, $TlPO_3$, there are two modifications: the first remaining as a slightly soluble vitreous mass when monothallious orthophosphate is strongly ignited, the second obtained as an easily soluble glass by igniting ammonio-thallious orthophosphate.

Thallic orthophosphate, $Tl'''PO_4.2H_2O$, separates as an insoluble gelatinous precipitate on diluting a solution of thallic nitrate mixed with phosphoric acid.

Thallium Sulphide, Tl_2S.—This compound is precipitated from all thallious salts by ammonium sulphide, and from the acetate, carbonate, or oxalate, by hydrogen sulphide (incompletely also from the nitrate, sulphate, or chloride), in dense flocks of a greyish or brownish-black colour. Thallic salts appear to be reduced to thallious salts by boiling with ammonium sulphide. Thallium sulphate projected into fused potassium cyanide is reduced to sulphide, which then forms a brittle metallic-looking mass, having the lustre of plumbago, and fusing more readily than metallic thallium.

Reactions of Thallium Salts.—The reactions of thallious salts with hydrogen sulphide and ammonium sulphide have just been mentioned. From their aqueous solutions thallium is rapidly precipitated in metallic crystals by *zinc*, slowly by *iron*. *Soluble chlorides* precipitate difficultly soluble white thallious chloride; soluble *bromides* throw down white, nearly insoluble bromide; soluble *iodides* precipitate insoluble yellow thallious iodide. *Caustic alkalis* and *alkaline carbonates* form no precipitate; *sodium phosphate* forms a white precipitate, insoluble in ammonia, easily soluble in acids.

Potassium chromate gives a yellow precipitate of thallious chromate, insoluble in cold nitric or sulphuric acid, but turning orange-red on boiling in the acid solution.—*Platinic chloride* precipitates a very pale-yellow insoluble double salt.

Thallic salts are easily distinguished from thallious salts by their behaviour with alkalis, and with soluble chlorides or bromides. Their solutions give with *ammonia*, and with *fixed alkalis* and their *carbonates*, a brown gelatinous precipitate of thallic oxide, containing the whole of the thallium. Soluble *chlorides* or *bromides* produce no precipitate in solutions of pure thallic salts; but if a thallious salt is likewise present, a precipitate of sesquichloride or sesquibromide is formed. *Oxalic acid* forms in solutions of thallic salts a white pulverulent precipitate; *phosphoric acid* a white gelatinous precipitate; and *arsenic acid* a yellow gelatinous precipitate. Thallic nitrate gives with *potassium ferrocyanide* a green, and with the *ferricyanide* a yellow precipitate.

In examining a mixed metallic solution, thallium will be found in the precipitate thrown down by ammonium sulphide, together with iron, nickel, manganese, &c. From these metals it may be easily separated by precipitation with potassium iodide or platinic chloride, or by reduction to the metallic state with zinc

Thallium salts are reduced before the blowpipe with charcoal and sodium carbonate or potassium cyanide. The green colour imparted to flame by thallium, and the peculiar character of its spectrum, have already been mentioned.

INDIUM.

Atomic weight, 113·4 Symbol, In.

THIS extremely rare metal was discovered in 1863 by Reich and Richter, in the zinc-blende of Freiberg, and has since been found in a few other zinc-ores and in the flue-dust of zinc furnaces. The metallic sponge which remains when the crude zinc of the Freiberg works is dissolved in dilute sulphuric acid, contains the whole of the indium (0·045 per cent.), together with lead, arsenic, cadmium, and iron. It is dissolved in nitric acid; the lead, arsenic, and cadmium are precipitated by hydrogen sulphide; and the filtered solution is heated with potassium chlorate to bring all the iron to the state of ferric salt, and then treated with ammonia, which precipitates the indium as a hydroxide, together with iron and zinc. The precipitate is dissolved in acetic acid; the indium is precipitated as sulphide by hydrogen sulphide; and freed from traces of iron and zinc by dissolving the precipitate in dilute hydrochloric acid, precipitating the indium by agitation with barium carbonate, dissolving out the indium hydroxide by dilute sulphuric acid, and reprecipitating with ammonia.

Indium, reduced from its oxide by ignition with sodium, is a silver-white metal, soft and ductile, has a specific gravity of 7·421, melts at 176°, and is less volatile than cadmium or zinc. When heated to redness in the air, it burns with a violet flame, and is converted into the yellow sesquioxide. Heated in chlorine, it burns with a yellow-green light, and forms a chloride, which sublimes without fusion at an incipient red heat in soft white laminæ.

Indium dissolves in the strong mineral acids, and is precipitated from the solutions by *zinc* and *cadmium*. *Hydrogen sulphide* precipitates it completely, as a yellow sulphide, from a solution of its acetate, and from neutral solutions of indium salts in general, but not from solutions containing excess of the strong mineral acids. *Ammonia* and *sodium carbonate* produce white precipitates insoluble in excess: *caustic potash* or *soda* throws down white indium hydroxide soluble in excess of the alkali. *Ammonium carbonate* forms a white precipitate soluble in excess, and reprecipitated on boiling. *Barium carbonate* precipitates indium completely.

The spectrum of indium is characterised by two indigo-coloured lines, one very bright and more refrangible than the blue line of strontium, the other fainter and still more refrangible, and approaching the blue line of potassium. It was the observation of this peculiar spectrum that led to the discovery of the metal.

The formulæ of the principal normal indium compounds are as follows:

Chloride, ...	$InCl_3$
Indium and Ammonium Chloride,	$2NH_4Cl.InCl_3 + H_2O$
Yellow Oxide, ...	In_2O_3
Hydroxide, ...	InH_3O_3
Nitrate, ...	$In(NO_3)_3$
Sulphate, ...	$In_2(SO_4)_3 + 9H_2O$.

The yellow oxide, heated in a stream of hydrogen, is successively reduced to a green, a grey, and a black oxide (InO_2), and at a low red heat to the metallic state.

GALLIUM.

Atomic weight, 68 (?) Symbol, Ga.

THIS metal was discovered in 1875 by Lecoq de Boisbaudran,* in a zinc-blende from the mine of Pierrefitte, in the valley of Argeles, Pyrenees, and has likewise been found, though always in very small quantity, in blendes from other localities. It is separated by dissolving the blende in nitromuriatic acid, immersing plates of zinc in the solution till the disengagement of hydrogen becomes slow,—whereby copper, lead, cadmium, and other metals are precipitated,—and then boiling the clear liquid for several hours with a large excess of zinc, which throws down alumina, basic zinc-salts, and oxide of gallium. This precipitate is redissolved in hydrochloric acid; the solution again boiled with zinc; the resulting precipitate, which contains the gallium in a more concentrated form, is redissolved in hydrochloric acid; the solution mixed with ammonium acetate is treated with hydrogen sulphide, which throws down the zinc and gallium as sulphides, leaving the aluminium in solution; and this treatment is repeated to ensure the complete separation of the alumina. The white sulphides of zinc and gallium are then dissolved in hydrochloric acid; the solution is fractionally precipitated with sodium carbonate, the gallium going down chiefly in the first portions; and, to complete the separation of the zinc, the gallium oxide is dissolved in sulphuric acid and reprecipitated by excess of ammonia; this dissolves all the zinc oxide, and the greater part of the gallium oxide, which may be reprecipitated by boiling the liquid to expel the free ammonia.

Metallic gallium is obtained by electrolysing a solution of the oxide in potash or ammonia with platinum electrodes, the gallium being deposited on the negative plate as a compact, closely adhering crust, which may be detached by bending the plate backwards and forwards under cold water.

Gallium is a hard metal somewhat whiter than platinum, and acquires a good polish by pressure; it is sectile and somewhat malleable;

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* Comptes Rendus, lxxxi. 493.

its specific gravity is 5·9, which is intermediate between that of aluminium (2·6) and that of indium (7·4). Its melting point is 30·1°, so that it liquefies when pressed between the fingers; frequently also it remains liquid for a long time even when cooled to nearly 0°. The melted metal adheres to glass, forming a mirror whiter than that produced by mercury. When heated to bright redness in contact with the air, it oxidises merely on the surface, and does not volatilise.

Gallium forms a very bright electric spectrum, exhibiting a brilliant line and a fainter band in the violet. In a gas-flame only the line is exhibited, and even this is very faint and fugitive. It was by these spectroscopic characters that the existence of gallium was first recognised.

Gallum chloride is very soluble and deliquescent. Its aqueous solution is clear when highly concentrated, but becomes turbid on addition of water; the precipitate (probably an oxychloride) dissolves but very slowly in hydrochloric acid. A slightly acidulated solution of the chloride evaporated at a gentle heat, deposits needles which act strongly on polarised light. The *sulphate* is not deliquescent.

Gallium forms an ammonia-alum, which crystallises in octohedrons like common alum; it dissolves in cold water, but the solution becomes turbid on boiling, and is decomposed by heating with acetic acid. The existence of this alum shows that the oxide of gallium is represented by the formula Ga_2O_3, and its chloride by $GaCl_3$.

Solutions of gallium salts give with *ammonium sulphide* a white precipitate of gallium sulphide insoluble in excess of the reagent. The same precipitate is formed by *hydrogen sulphide* in presence of acetic, but not of hydrochloric acid. *Ammonia* and *carbonate of ammonia* give white precipitates soluble in excess. Slightly acid solutions of the chloride and sulphate are not precipitated in the cold by *ammonium acetate;* but the neutral solutions are clouded thereby. Gallium oxide is easily precipitated by *barium carbonate.*

In a mixed solution of gallium and aluminium, the latter is precipitated before the gallium, and in a mixed solution of gallium and indium, the gallium goes down first; in point of basicity, therefore, gallium is intermediate between aluminium and indium.

The atomic weight of gallium has not been determined by direct experiment; but as this metal is a triad intermediate in some of its properties (basicity and density) between aluminium and indium, and in its chemical reactions exhibits considerable resemblance to zinc, it is supposed to have an atomic weight not far from 68, as assigned to it in Mendelejeff's Classification of the Elements (p. 265).

TETRAD METALS.

TIN.

Atomic weight, 118. Symbol, Sn (Stannum).

THIS valuable metal occurs in the state of oxide, and more rarely as sulphide: the principal tin mines are those of Saxony and Bohemia, Malacca, and more especially Cornwall. In Cornwall the tin-stone is found as a constituent of metal-bearing veins, associated with copper ore, in granite and slate-rocks; and as an alluvial deposit, mixed with rounded pebbles, in the beds of several small rivers The first variety is called *mine-* and the second *stream-tin.* Tin oxide is also found disseminated through the rock itself in small crystals.

To prepare the ore for reduction, it is stamped to powder, washed, to separate as much as possible of the earthy matter, and roasted, to expel sulphur and arsenic: it is then strongly heated with coal, and the metal thus obtained is cast into large blocks. Two varieties of commercial tin are known, called *grain-* and *bar-tin;* the first is the best; it is prepared from the stream ore.

Pure tin has a white colour, approaching that of silver: it is soft and malleable, and when bent or twisted emits a peculiar crackling sound; it has a density of 7·3, and melts at 237°. Tin is but little acted upon by air and water, even conjointly; when heated above its melting-point, it oxidises rapidly, becoming converted into a whitish powder, used in the arts for polishing, under the name of *putty powder.* The metal is attacked and dissolved by hydrochloric acid, with evolution of hydrogen; nitric acid acts with great energy, converting it into a white hydrate of the dioxide.

Tin is a tetrad metal, and forms two well-defined classes of compounds, namely, the stannous compounds, in which it is bivalent, as $SnCl_2$, SnI_2, SnO, &c., and the stannic compounds, in which it is quadrivalent, as $SnCl_4$, SnO_2, &c.; also a few compounds called stannoso-stannic compounds, of intermediate composition, *e.g.*, Sn_2Cl_6, Sn_2O_3, &c.

Chlorides.—The *dichloride*, or *Stannous chloride*, $SnCl_2$, is obtained in the anhydrous state by distilling a mixture of calomel and powdered tin, prepared by agitating the melted metal in a wooden box until it solidifies. It is a grey, resinous-looking substance, fusible below redness, and volatile at a high temperature.

The *hydrated chloride*, commonly called *tin salt*, is easily prepared by dissolving metallic tin in hot hydrochloric acid. It crystallises in needles containing $SnCl_2.2H_2O$, which are freely soluble in a small quantity of water, but are apt to be decomposed in part when put into a large mass, unless hydrochloric acid in excess be present. Solution of stannous chloride is employed as a deoxidising agent; it reduces the salts of mercury and other metals of the same class. It is also extensively employed as a mordant in dyeing and calico-printing; sometimes also as an antichlore.

Stannous chloride unites with the chlorides of the alkali-metals, forming crystallisable double salts, $SnCl_2.2KCl$, &c., called *Stannoso-chlorides* or *Chlorostannites*.

The *tetrachloride*, or *Stannic chloride*, $SnCl_4$, formerly called *fuming liquor of Libavius*, is made by exposing metallic tin to the action of chlorine, or, more conveniently, by distilling a mixture of 1 part of powdered tin with 5 parts of corrosive sublimate. It is a thin, colourless, mobile liquid, boiling at 120°, and yielding a colourless invisible vapour. It fumes in the air, and when mixed with a third part of water, solidifies to a soft fusible mass, called *butter of tin*. The solution of stannic chloride is much employed by the dyer for the brightening and fixing of red colours, and is sometimes designated by the old names, "composition, physic, or tin solution;" it is commonly prepared by dissolving metallic tin in a mixture of hydrochloric and nitric acids, care being taken to avoid too great elevation of temperature. The solution when evaporated yields a deliquescent crystalline hydrate, $SnCl_4.5H_2O$.

Stannic chloride forms, with the chlorides of the alkali-metals and alkaline earth-metals, crystalline double salts, called *Stannochlorides* or *Chlorostannates*, *e.g.*, $SnCl_4.2NH_4Cl$; $SnCl_4.BaCl_2$, &c. It also forms crystalline compounds with the pentachloride and oxychloride of phosphorus, viz., $SnCl_4.PCl_5$, and $SnCl_4.POCl_3$, and a solid compound with phosphine, containing $3SnCl_4.2PH_3$.

The *trichloride*, or *Stannoso-stannic chloride*, known only in solution, is produced by dissolving the sesquioxide in hydrochloric acid. The solution acts like a mixture of the dichloride and tetrachloride.

Fluorides.—*Stannous Fluoride*, SnF_2, obtained by evaporating the solution of stannous oxide in hydrofluoric acid, crystallises in small shining opaque prisms. *Stannic fluoride*, SnF_4, is not known in the free state, but unites with other metallic fluorides, forming crystalline compounds, called *stannofluorides* or *fluostannates*, isomorphous with the corresponding silicofluorides, titanofluorides, and zircofluorides. The potassium salt contains $SnF_4.2KF.H_2O$, the barium salt, $SnF_4.BaF_2$, &c.

Oxides.—The *monoxide* or *Stannous oxide*, SnO, is produced by heating stannous oxalate out of contact with the air; also by igniting stannous hydrate. This *hydrate*, $2SnO.H_2O$, or $Sn_2H_2O_3$, is obtained as a white precipitate by decomposing stannous chloride with an alkaline carbonate, carbon dioxide gas being at the same time evolved. This hydrate, carefully washed, dried, and heated in an atmosphere of carbon dioxide, leaves anhydrous stannous oxide as a dense black powder, which is permanent in the air, but when touched with a red-hot body, takes fire and burns like tinder, producing the dioxide. The hydrate is freely soluble in caustic potash,

or cassiterite, the common ore of tin, and
tin, stannous oxide, or stannous hydrate i
thus prepared it is a white or yellowish a
passing the vapour of stannic chloride m
through a red-hot porcelain tube, it may
is not attacked by acids, even in the conc
Stannic oxide forms two hydrates, diff
composition and properties ; both, howeve
of forming salts by exchanging their hy
hydrates or acids are stannic acid, S
metastannic acid, $Sn_5O_{10}.5H_2O$, or H
capable of exchanging the whole of its
forming the stannates, containing M
exchanges only one-fifth of its hydrogen
nates, $H_8M_2Sn_5O_{15}$.

Stannic acid is precipitated by acids f
stannates, also from solution of stannic
barium carbonate not in excess ; alkaline
acid stannate. When dried in the air at
has, according to Weber, the composition
half the water is given off, leaving $SnO_2.H$

Stannic hydrate dissolves in the stro
stannic salts ; thus with sulphuric acid i
$Sn(SO_4)_2$ or $SnO.2SO_3$. *Hydrochloric ac*
tetrachloride. The stannic salts of oxygen

Stannates.—Stannic hydrate exhibits a
than basic properties. It forms easily solu
and from these the insoluble stannates of th
metals may be obtained by precipitation. *S*
which is much used in calico-printing a

crystalline powder insoluble in water and in acids. It dissolves slowly in alkalis, forming metastannates, but it is gradually deposited in its original state as the solution absorbs carbonic acid from the air. The *potassium salt*, $K_2H_8Sn_5O_{15}$ or $\left.\begin{matrix}K_2O\\4H_2O\end{matrix}\right\}(SnO_2)_5$, may be precipitated in the solid state by adding pieces of solid potash to a solution of metastannic acid in cold potash. It is gummy, uncrystallisable, and strongly alkaline. The *sodium salt*, $Na_2H_8SnO_{15}$, prepared in like manner, is crystallo-granular, and dissolves slowly, but completely, in water. The metastannates exist only in the hydrated state, being decomposed when deprived of their basic water.

Tin Sulphides.—The *monosulphide*, SnS, is prepared by fusing tin with excess of sulphur, and strongly heating the product. It is a lead-grey, brittle substance, fusible at a red heat, and soluble, with evolution of sulphuretted hydrogen, in hot hydrochloric acid. A *sesquisulphide* may be formed by gently heating the above compound with a third of its weight of sulphur: it is yellowish-grey, and easily decomposed by heat. The *bisulphide*, SnS_2, or *Mosaic gold*, is prepared by exposing to a low red heat, in a glass flask, a mixture of 12 parts of tin, 6 of mercury, 6 of sal-ammoniac, and 7 of flowers of sulphur. Sal-ammoniac, cinnabar, and stannous chloride sublime, while the bisulphide remains at the bottom of the vessel in the form of brilliant gold-coloured scales: it is used as a substitute for gold powder. The same compound is obtained as an amorphous light-yellow powder by passing hydrogen sulphide into a solution of stannic chloride.

Stannous salts give with:

Fixed caustic alkalis: white hydrate, soluble in excess.

Ammonia: carbonates of potassium, sodium, and *ammonium*, . } white hydrate, nearly insoluble in excess.

Hydrogen sulphide, .
Ammonium sulphide, . } black-brown precipitate of monosulphide, soluble in ammonium sulphide containing excess of sulphur, and reprecipitated by acids as yellow bisulphide.

Stannic salts give with:

Fixed caustic alkalis: white hydrate, soluble in excess.
Ammonia: white hydrate, slightly soluble in excess.
Alkaline carbonates: white hydrate, slightly soluble in excess.
Ammonium carbonate: white hydrate, insoluble.
Hydrogen sulphide: yellow precipitate of bisulphide.
Ammonium sulphide: the same, soluble in excess.

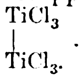
Trichloride of gold, added to a dilute solution of stannous chloride, gives rise to a brownish-purple precipitate, called *purple of Cassius* (p 418).

The useful applications of tin are very numerous. *Tinned plate* consists of iron superficially alloyed with this metal; *pewter*, of the best kind, is chiefly tin, hardened by the admixture of a little antimony, &c. Cooking-vessels of copper are usually tinned in the interior. The use of tin solutions in dyeing and calico-printing has been already mentioned.

TITANIUM.

Atomic weight, 50. Symbol, Ti.

THIS is one of the rarer metals, and is never found in the metallic state. The most important titanium minerals are *rutile*, *brookite*, and *anatase*, which are different forms of titanic oxide, and the several varieties of titaniferous iron, consisting of ferrous titanate, sometimes alone, but more generally mixed with ferric or ferroso-ferric oxide. Occasionally in the slag adhering to the bottom of blast-furnaces in which iron ore is reduced, small brilliant copper-coloured cubes, hard enough to scratch glass, and in the highest degree infusible, are found. This substance, of which a single smelting furnace in the Hartz produced as much as 80 pounds, was formerly believed to be metallic titanium. Wöhler, however, has shown it to be a combination of titanium cyanide with titanium nitride. When these crystals are powdered, mixed with potassium hydrate, and fused, ammonia is evolved, and potassium titanate is formed. Metallic titanium in a finely divided state may be obtained by heating titanium and potassium fluoride with potassium. This element is remarkable for its affinity for nitrogen: when heated in the air, it simultaneously absorbs oxygen and nitrogen.

Titanium is tetradic, like tin, and forms two classes of compounds: the titanic compounds, in which it is quadrivalent, *e.g.*, $TiCl_4$, TiO_2, and the titanous compounds, in which it is apparently trivalent, but really also quadrivalent, *e.g.*, Ti_2Cl_6, or  $\begin{array}{c} TiCl_3 \\ | \\ TiCl_3 \end{array}$.

Chlorides.—*Titanous chloride*, Ti_2Cl_6, is produced by passing the vapour of titanic chloride mixed with hydrogen through a red-hot tube; it forms dark violet scales having a strong lustre. *Titanic chloride* $TiCl_4$, is prepared by passing chlorine over an ignited mixture of titanic oxide and charcoal. It is a colourless, volatile, fuming liquid, having a specific gravity of 1·7609 at 0°, vapour-density = 6·658, and boiling at 135°. It unites very violently with water, and forms definite compounds with ammonia, ammonium chloride, hydrogen cyanide, cyanogen chloride, phosphine, and sulphur tetrachloride.

Fluorides.—*Titanous fluoride*, Ti_2F_6, is obtained as a violet powder by igniting potassio-titanic fluoride in hydrogen gas, and treating the resulting mass with hot water. *Titanic fluoride*, TiF_4, passes over as a fuming colourless liquid, when titanic oxide is distilled with fluor-spar and fuming sulphuric acid in a platinum apparatus. It unites with hydrofluoric acid and metallic fluorides, forming double salts called titano-fluorides or fluotitanates, isomorphous with the silicofluorides, zircofluorides, &c., *e.g.*, $TiF_4.2KF$; $TiF_4.CaF_2$.

Oxides.—The *sesquioxide*, or *Titanous oxide*, Ti_2O_3, is obtained by igniting the dioxide in hydrogen, as a black powder, which, when heated in the air to a very high temperature, oxidises to titanic oxide.

The *dioxide*, or *Titanic oxide*, occurs native in three different forms, viz., as rutile and anatase, which are dimetric, and brookite, which is trimetric; of these anatase is the purest, and rutile the most abundant. To obtain pure titanic oxide, rutile or titaniferous iron ore, reduced to fine powder, is fused with twice its weight of potassium carbonate, and the fused mass is dissolved in dilute hydrofluoric acid, whereupon titano-fluoride of potassium soon begins to separate. From the hot aqueous solution of this salt, ammonia throws down snow-white ammonium titanate, which is easily soluble in hydrochloric acid, and when ignited gives reddish-brown lumps of titanic oxide. This oxide is insoluble in water, and in all acids except strong sulphuric acid. By fusing it with six times its weight of acid potassium sulphate, a clear yellow mass is obtained, which dissolves perfectly in warm water.

Titanic oxide appears to form two hydrates or acids, analogous to stannic and metastannic acids. One of these, called titanic acid, is precipitated by ammonia from a solution of titanic chloride, as a white powder which dissolves easily in sulphuric, nitric, and hydrochloric acids, even when these acids are rather dilute; but these dilute solutions, when boiled, deposit metatitanic hydrate as a soft white powder, which, like the anhydrous oxide, is insoluble in all acids except strong sulphuric acid.

The titanates have not been much studied; most of them may be represented by the formulæ $M_4TiO_4 = 2M_2O.TiO_2$, and $M_2TiO_3 = M_2O.TiO_2$ (the symbol M denoting a univalent metal). The titanates of calcium and iron occur as natural minerals. The titanates of the alkali-metals are formed by fusing titanic oxide with alkaline hydrates, carbonates, or acid sulphates—some of them also in the wet way. When finely pulverised and levigated, they dissolve in moderately warm, concentrated hydrochloric acid; but the greater part of the dissolved titanic acid is precipitated on boiling the solution with dilute acids. The neutral titanates of the alkali-metals, M_2TiO_3, are insoluble in water, but soluble in acids. The titanates of the earth-metals and heavy metals are insoluble, and may be obtained by precipitation.

In a solution of titanic acid in hydrochloric acid, containing as little free acid as possible, *tincture of galls* produces an orange-coloured precipitate; *potassium ferrocyanide*, a dark brown preci-

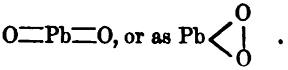
Atomic weight, 207. Symbol,

THIS abundant and useful metal is alt native sulphide, or *galena*, no other lead quantity. The reduction is effected in a which the crushed lead-ore is introduced at a dull red heat, by which much of the by oxidation to sulphate. The contents thoroughly mixed, and the temperature and sulphide react upon each other, produc metallic lead:

$$PbSO_4 + PbS = Pb_2 +$$

Lead is a soft bluish metal, possessing specific gravity is 11·45. It may be easily drawn out into coarse wires, but has very at 315·5°, or a little above, and boils and v By slow cooling, it may be obtained in moist air this metal becomes coated with thought to be suboxide, and when exposed melted state it rapidly absorbs oxygen. D ception of nitric acid, act but slowly upon l

Lead is a tetrad, as shown by the constit $Pb(C_2H_5)_4$; but in its inorganic combina forming but one chloride, $PbCl_2$, with cor iodide. The oxide corresponding with these higher oxides in which the metal may be r or as a tetrad: thus the dioxide PbO_2 may



$\mathrm{O{=}Pb{=}O}$, or as $\mathrm{Pb}<\begin{matrix}\mathrm{O}\\ |\\ \mathrm{O}\end{matrix}$.

acid, dissolving the resulting chloride in hot water, and precipitating with lime-water. A third oxychloride, $PbCl_2.7PbO$, called *patent yellow* or *Turner's yellow*, is prepared by heating 1 part of sal-ammoniac with 10 parts of litharge.

Lead Iodide, PbI_2, is precipitated, on mixing lead nitrate or acetate with potassium iodide, as a bright yellow powder, which dissolves in boiling water, and crystallises therefrom in beautiful yellow iridescent spangles.

Oxides.—The *monoxide*, PbO, called *litharge* or *massicot*, is the product of the direct oxidation of the metal. It is most conveniently prepared by heating the carbonate to dull redness; common *litharge* is impure monoxide which has undergone fusion. Lead oxide has a delicate straw-yellow colour, is very heavy, and slightly soluble in water, giving an alkaline liquid. It is soluble in potash, and crystallises from the solution in rhombic prisms. At a red heat it melts, and tends to crystallise on cooling. In the melted state it attacks and dissolves silicious matter with astonishing facility, often penetrating an earthen crucible in a few minutes. It is easily reduced when heated with organic substances of any kind containing carbon or hydrogen. It forms a large class of salts, often called *plumbic salts*, which are colourless if the acid itself is not coloured.

Triplumbic tetroxide, or *Red lead*, is not of very constant composition, but generally contains Pb_3O_4 or $2PbO.PbO_2$. It is prepared by exposing the monoxide, which has not been fused, for a long time to the air, at a very faint red heat; it is a brilliant red and extremely heavy powder, decomposed, with evolution of oxygen, by a strong heat, and converted by acids into a mixture of monoxide and dioxide. It is used as a cheap substitute for vermilion.

The *dioxide*, PbO_2, often called *puce* or *brown lead-oxide*, is obtained without difficulty by digesting red lead in dilute nitric acid, whereby lead nitrate is dissolved out, and insoluble dioxide left behind in the form of a deep-brown powder. The dioxide is decomposed by a red heat, yielding up one-half of its oxygen. Hydrochloric acid converts it into lead chloride, with disengagement of chlorine; hot oil of vitriol forms with it lead sulphate, and liberates oxygen. The dioxide is very useful in separating sulphurous acid from certain gaseous mixtures, lead sulphate being then produced: $PbO_2+SO_2=PbSO_4$.

Diplumbic oxide, or *Lead suboxide*, Pb_2O, is formed when the monoxide is heated to dull redness in a retort: a grey pulverulent substance is then left, which is resolved by acids into monoxide and metal. It absorbs oxygen with great rapidity when heated, and even when simply moistened with water and exposed to the air.

Lead Nitrate, $Pb(NO_3)_2$, or $PbO.N_2O_5$, may be obtained by dissolving lead carbonate in nitric acid, or by acting directly upon the metal by the same agent with the aid of heat: it is, as already noticed, a bye-product in the preparation of the dioxide. It crystallises in anhydrous octohedrons, which are usually milk-white and opaque. It dissolves in 7½ parts of cold water, and is decomposed by heat, yielding nitrogen tetroxide, oxygen, and lead monoxide, which obstinately retains traces of nitrogen. When a solution of this salt is boiled with an additional quantity of lead oxide, a portion of the latter is dissolved, and a basic nitrate generated, which may be obtained in crystals. Carbonic acid separates this excess of oxide in the form of a white compound of carbonate and hydrate of lead.

Neutral and basic compounds of lead oxide with the trioxide and tetroxide of nitrogen, have been described. These last are probably formed by the combination of a nitrite with a nitrate.

Lead Carbonate; *White Lead;* $PbCO_3$ or $PbO.CO_2$.—This salt is sometimes found beautifully crystallised in long white needles, accompanying other metallic ores. It may be prepared artificially by precipitating in the cold a solution of the nitrate or acetate with an alkaline carbonate: when the lead solution is boiling, the precipitate is a basic salt containing $2PbCO_3.PbH_2O_2$. It is also manufactured to an immense extent by other means for the use of the painter. Pure lead carbonate is a soft white powder, of great specific gravity, insoluble in water, but easily dissolved by dilute nitric or acetic acid. Of the many methods put in practice, or proposed, for making white lead, the two following are the most important and interesting. One of these consists in forming a basic nitrate or acetate of lead by boiling finely powdered litharge with the neutral salt. This solution is then brought into contact with carbonic acid gas, whereby all the excess of oxide previously taken up by the neutral salt is at once precipitated as white lead. The solution strained or pressed from the latter is again boiled with litharge, and treated with carbonic acid: these processes are susceptible of indefinite repetition, whereby the little loss of neutral salt left in the precipitates is compensated. The second, and by far the more ancient method, is rather more complex, and at first sight not very intelligible. A great number of earthen jars are prepared, into each of which is poured a few ounces of crude vinegar; a roll of sheet lead is then introduced in such a manner that it shall neither touch the vinegar nor project above the top of the jar. The vessels are next arranged in a large building, side by side, upon a layer of stable manure, or, still better, spent tan, and closely covered with boards. A second layer of tan is spread upon the top of the latter, and then a second series of pots; these are in turn covered with boards and decomposing bark, and in this manner a pile of many alternations is constructed. After the lapse of a considerable time, the pile is taken down and the sheets of lead are removed and carefully unrolled; they are then found to be in great part converted into carbonate, which merely requires washing and grinding to be fit for use. The nature of this curious process is generally explained by supposing the vapour of vinegar raised by the high temperature of the fermenting matter, merely to act as a carrier between the carbonic acid evolved from the tan and the lead oxide formed under the influence of the acid vapour, a neutral acetate, a basic acetate, and a carbonate being produced in succession, and the action gradually travelling from the surface inwards. The quantity of acetic acid used is, in relation to the lead, quite trifling, and cannot directly contribute to the production of the carbonate. A preference is still given to the product of this old mode of manufacture, on account of its superior opacity, or *body*, over that obtained by precipitation. Commercial white lead, however prepared, always contains a certain proportion of hydrate. It is sometimes adulterated with barium sulphate.

When clean metallic lead is put into pure water and exposed to the air, a white, crystalline, scaly powder begins to show itself in a few hours, and very rapidly increases in quantity. This substance may consist of lead hydrate, formed by the action of the oxygen dissolved in the water upon the lead. It is slightly soluble, and may be readily detected in the water. In most cases, however, the formation of this deposit is due to the action of the carbonic acid dissolved in the water : it consists of carbonate in combination with hydrate, and is nearly insoluble in water. When common river or spring water is substituted for the pure liquid, this effect is less observable, the little sulphate, almost invariably present, causing the deposition of a very thin but closely adherent film of lead sulphate upon the surface of the metal, which protects it from further action. It is on this account that leaden cisterns are used with impunity, at least in most cases, for holding water: if the latter were quite pure, it would be speedily contaminated with lead, and the cistern would be soon destroyed. Natural water highly charged with carbonic acid cannot, under any circumstances, be kept in lead or passed through leaden pipes with safety, the carbonate, though insoluble in pure water, being slightly soluble in water containing carbonic acid.

The soluble salts of lead behave with reagents as follows :—

Caustic *potash* and *soda* precipitate a white hydrate freely soluble in excess. Ammonia gives a similar white precipitate, not soluble in excess. The *carbonates of potassium, sodium,* and *ammonium* precipitate lead carbonate, insoluble in excess. *Sulphuric acid* or a *sulphate* causes a white precipitate of lead sulphate, insoluble in nitric acid. *Hydrogen sulphide* and *ammonium sulphide* throw down black lead sulphide. Lead is readily detected before the blowpipe by fusing the compound under examination on charcoal with sodium carbonate, when a bead of metal is easily obtained, which is recognised by its chemical as well as physical properties.

An alloy of 2 parts of lead and 1 of tin constitutes *plumbers' solder*; these proportions reversed give a more fusible compound, called *fine solder*. The lead employed in the manufacture of shot is combined with a little arsenic.

THIS important metal is found chiefly in
ore is freed by fusion from earthy in
decomposed by heating with metallic i
which retains the sulphur.

Antimony has a bluish-white colou
extremely brittle, being reduced to pow
Its specific gravity is 6·8 ; it melts at a
redness, and boils and volatilises at a
a distinct, crystalline, platy structure, but
it may be obtained in crystals, which are
oxidised by the air at common temperatu
it burns with a white flame, produci
deposited in beautiful crystals. It is dis
acid, with evolution of hydrogen and prod
acid oxidises it to antimonic acid, which i

Antimony forms two classes of compou
pounds in which it is trivalent, as $SbCl_3$,
antimonic compounds in which it is quinq
Sb_2S_5, &c.

Chlorides.—The *trichloride* or *Anti*
formerly called *butter of antimony*, is p
sulphide is prepared by the action of str
antimonious sulphide. The impure and
obtained is put into a retort and distilled,
densed product, on falling into the aqueo
produces a copious white precipitate. The
and the distillation continued. Pure an
passes over, and solidifies on cooling to a
mass, from which the air must be careful
compound is formed by distilli

of Algaroth; it is a compound of trichloride and trioxide of antimony. Alkaline solutions extract the chloride and leave the oxide. Finely powdered antimony thrown into chlorine gas takes fire.

The *Pentachloride* or *Antimonic chloride*, $SbCl_5$, is formed by passing a stream of chlorine gas over gently heated metallic antimony: a mixture of the two chlorides results, which may be separated by distillation. The pentachloride is a colourless volatile liquid, which forms a crystalline compound with a small portion of water, but is decomposed by a larger quantity into antimonic and hydrochloric acids.

Antimonious Hydride. Antimonetted Hydrogen. Stibine, SbH_3.—When zinc is put into a solution of antimonious oxide, and sulphuric acid added, part of the hydrogen combines with the antimony, and the resulting gas, which is a mixture of stibine with free hydrogen, burns with a greenish flame, giving rise to white fumes of antimonious oxide. When the gas is conducted through a red-hot glass tube of narrow dimensions, or burned with a limited supply of air, as when a cold porcelain surface is pressed into the flame, metallic antimony is deposited. On passing a current of antimonetted hydrogen through a solution of silver nitrate, a black precipitate is obtained, containing $SbAg_3$: from the formation of this compound it is inferred that the gas has the composition SbH_3, analogous to ammonia, phosphine, and arsine. There are also several analogous compounds of antimony with alcohol-radicles, such as *trimethylstibine*, $Sb(CH_3)_3$, *triethylstibine*, $Sb(C_2H_5)_3$, &c.

Oxides.—Antimony forms two oxides, Sb_2O_3 and Sb_2O_5, analogous to the chlorides, the first being a basic and the second an acid oxide, also an intermediate neutral oxide, Sb_2O_4. The *trioxide*, or *Antimonious oxide*, Sb_2O_3, occurs native, though rarely, as *valentinite*, or *white antimony*, in shining white trimetric crystals; also as *senarmontite* in regular octohedrons: it is therefore dimorphous. It may be prepared by several methods: as by burning metallic antimony at the bottom of a large red-hot crucible, in which case it is obtained in brilliant crystals; or by pouring solution of antimonious chloride into water, and digesting the resulting precipitate with a solution of sodium carbonate. The oxide thus produced is anhydrous; it is a pale buff-coloured powder, fusible at a red heat, and volatile in a closed vessel, but in contact with air at a high temperature, it absorbs oxygen and becomes changed into the tetroxide. When boiled with cream of tartar (acid potassium tartrate), it is dissolved, and the solution yields on evaporation crystals of *tartar emetic*, which is almost the only antimonious salt that can bear admixture with water without decomposition. An impure oxide for this purpose is sometimes prepared by carefully roasting the powdered sulphide in a reverberatory furnace, and raising the heat at the end of the process, so as to fuse the product: it has long been known under the name *glass of antimony*, or *vitrum antimonii*.

Antimonious oxide likewise acts as a feeble acid, forming salts called *antimonites* which, however, are very unstable.

The *tetroxide*, or *Antimonoso-antimonic oxide*, Sb_2O_4 or $Sb_2O_3.Sb_2O_5$, occurs native as *cervantite*, or *antimony ochre*, in acicular crystals, or as a crust or powder. It is the ultimate product of the oxidation of the metal by heat and air: it is a greyish-white powder, infusible and non-volatile, insoluble in water and acids, except when recently precipitated. On treating it with tartaric acid (acid potassium tartrate), antimonious oxide is dissolved, antimonic acid remaining behind; and when a solution of the tetroxide in hydrochloric acid is gradually dropped into a large quantity of water, antimonious oxide is precipitated, while antimonic acid remains dissolved. From these and similar reactions it has been inferred that the tetroxide is a compound of the trioxide and pentoxide. On the other hand, it is sometimes regarded as a distinct oxide, because it dissolves without decomposition in alkalis, forming salts (often called *antimonites*) which may be obtained in the solid state. Two potassium salts, for example, have been formed, containing $K_2O.Sb_2O_4$ and $K_2O.2Sb_2O_4$; and a calcium salt, $3CaO.2Sb_2O_4$, occurs as a natural mineral, called *romeine*. These salts may, however, be regarded as compounds of antimonates and antimonites (containing Sb_2O_3): thus, $2(K_2O.Sb_2O_4) = K_2O.Sb_2O_5 + K_2O.Sb_2O_3$.

The *pentoxide*, or *Antimonic oxide*, Sb_2O_5, is formed as an insoluble hydrate when strong nitric acid is made to act upon metallic antimony; and, on exposing this hydrate to a heat short of redness, it yields the anhydrous pentoxide as a pale straw-coloured powder, insoluble in water and acids. It is decomposed by a red heat, yielding the tetroxide.

Hydrated antimonic oxide is likewise obtained by decomposing antimony pentachloride with an excess of water, hydrochloric acid being formed at the same time. The hydrated oxides, or acids, produced by the two processes mentioned, differ in many of their properties, and especially in their deportment with bases. The acid produced by nitric acid, called antimonic acid, is monobasic, producing normal salts of the form $M_2O.Sb_2O_5$ or $MSbO_3$, and acid salts, containing $M_2O.2Sb_2O_5$ or $2MSbO_3.Sb_2O_5$. The other, called metantimonic acid, is bibasic, forming normal salts containing $2M_2O.Sb_2O_5$ or $M_4Sb_2O_7$, and acid salts containing $2M_2O.2Sb_2O_5$ or $M_2O.Sb_2O_5$, so that the acid metantimonates are isomeric or polymeric with the normal antimonates. Among the metantimonates an acid potassium salt, $K_2O.Sb_2O_5.7H_2O$, is to be particularly noticed as yielding a precipitate with sodium salts: it is, indeed, the only reagent which precipitates sodium. It is obtained by fusing antimonic oxide with an excess of potash in a silver crucible, dissolving the fused mass in a small quantity of cold water, and allowing it to crystallise in a vacuum. The crystals consist of normal potassium metantimonate, $2K_2O.Sb_2O_5$, and, when dissolved in pure water, are decomposed into free potash and acid metantimonate.

Sulphides.—The *trisulphide*, or *Antimonious sulphide*, Sb_2S_3, occurs native as a lead-grey, brittle substance, having a radiated crystalline texture, and easily fusible. It may be prepared artificially by melting together antimony and sulphur. When a solution of tartar-emetic is precipitated by hydrogen sulphide, a brick-red precipitate falls, which is the same substance combined with a little water. If the precipitate be dried and gently heated, the water may be expelled without other change of colour than a little darkening, but at a higher temperature it assumes the colour and aspect of the native sulphide. This remarkable change probably indicates a passage from the amorphous to the crystalline state. When powdered antimonious sulphide is boiled in a solution of caustic potash, it is dissolved, antimonious oxide and potassium sulphide being produced; and the latter unites with an additional quantity of antimonious sulphide to form a soluble sulphur-salt, in which the potassium sulphide is the sulphur-base, and the antimonious sulphide is the sulphur-acid :

$$3K_2O + 2Sb_2S_3 = Sb_2O_3 + 3K_2S.Sb_2S_3 .$$

The antimonious oxide separates in small crystals from the boiling solution when the latter is concentrated, and the sulphur-salt dissolves an extra portion of antimonious sulphide, which it again deposits on cooling as a red amorphous powder, containing a small admixture of antimonious oxide and potassium sulphide. This is the *kermes mineral* of the old chemists. The filtered solution mixed with an acid gives a potassium salt, hydrogen sulphide, and precipitated antimonious sulphide. Kermes may also be made by fusing a mixture of 5 parts antimonious sulphide and 3 of dry sodium carbonate, boiling the mass in 80 parts of water, and filtering while hot : the compound separates on cooling. The compounds of antimonious sulphide with basic sulphides are called *sulphantimonites;* many of them occur as natural minerals. For example : zinkenite, $PbS.Sb_2S_3$; feather-ore, $2PbS.Sb_2S_3$; boulangerite, $3PbS.Sb_2S_3$; fahlore, or tetrahedrite, $4Cu_2S.Sb_2S_3$, the antimony being more or less replaced by arsenic, and the copper by silver, iron, zinc, and mercury.

The *pentasulphide*, or *Antimonic sulphide*, Sb_2S_5, formerly called *sulphur auratum*, is also a sulphur-acid, forming salts called *sulphantimonates*, most of which have the composition $3M_2S.Sb_2S_5$ or M_3SbS_4, analogous to the normal orthophosphates and arsenates. When 18 parts of finely powdered antimonious sulphide, 17 parts dry sodium carbonate, 13 parts slaked lime, and 3½ parts sulphur, are boiled in water for some hours, calcium carbonate, sodium antimonate, antimony pentasulphide, and sodium sulphide are produced. The first is insoluble, and the second partially so : the two last-named bodies, on the contrary, unite to form soluble sodium sulphantimonate, Na_3SbS_4, which may be obtained by evaporation in beautiful crystals. A solution of this substance, mixed with dilute sulphuric acid, furnishes sodium sulphate, hydrogen sulphide, and antimony pentasulphide, which falls as a golden-yellow flocculent precipitate.

The sulphantimonates of the alkali-metals and alkaline earth metals are very soluble in water, and crystallise for the most part with several molecules of water. Those of the heavy metals are insoluble, and are obtained by precipitation.

The few salts of antimony soluble in water are distinctly characterised by the orange or brick-red precipitate with *hydrogen sulphide*, which is soluble in a solution of ammonium sulphide, and again precipitated by an acid.

Antimonious chloride, as already observed, is decomposed by *water*, yielding a precipitate of oxychloride. The precipitate dissolves in hydrochloric acid, and the resulting solution gives, with *potash*, a white precipitate of trioxide, soluble in a large excess of the reagent; with *ammonia* the same, insoluble in excess; with *potassium* or *sodium carbonate*, also a precipitate of trioxide, which dissolves in excess, especially of the potassium salt, but reappears after a while. If, however, the solution contains *tartaric acid*, the precipitate formed by potash dissolves easily in excess of the alkali; ammonia forms but a slight precipitate, and the precipitates formed by alkaline carbonates are insoluble in excess. The last mentioned characters are likewise exhibited by a solution of tartar-emetic (potassio-antimonious tartrate). *Zinc* and *iron* precipitate antimony from its solutions as a black powder. *Copper* precipitates it as a shining metallic film, which may be dissolved off by potassium permanganate, yielding a solution which will give the characteristic red precipitate with hydrogen sulphide.

Solid antimony-compounds, fused upon charcoal with sodium carbonate or potassium cyanide, yield a brittle globule of antimony, a thick white fume being at the same time given off, and the charcoal covered to some distance around with a white deposit of oxide.

Besides its application to medicine, antimony is of great importance in the arts, inasmuch as, in combination with lead, it forms *type-metal*. This alloy expands at the moment of solidifying, and takes an exceeding sharp impression of the mould. It is remarkable that both its constituents shrink under similar circumstances, and make very bad castings.

Britannia metal is an alloy of 9 parts tin and 1 part antimony, frequently also containing small quantities of copper, zinc, or bismuth. An alloy of 12 parts tin, 1 part antimony, and a small quantity of copper, forms a superior kind of pewter. Alloys of antimony with tin, or tin and lead, are now much used for machinery-bearings in place of gun-metal. Alloys of antimony with nickel and with silver occur as natural minerals.

Antimony trisulphide enters into the composition of the blue signal-lights used at sea.*

ARSENIC.

Atomic weight, 75. Symbol, As.

ARSENIC is sometimes found native: it occurs in considerable quantity as a constituent of many minerals, combined with metals, sulphur and oxygen. In the oxidised state, it has been found in very minute quantity in a great many mineral waters. The largest proportion is derived from the roasting of natural arsenides of iron, nickel, and cobalt. The operation is conducted in a reverberatory furnace, and the volatile products are condensed in a long and nearly horizontal chimney, or in a kind of tower of brickwork, divided into numerous chambers. The crude arsenious oxide thus produced is purified by sublimation, and then heated with charcoal in a retort; the metal is reduced, and readily sublimes.

Arsenic has a steel-grey colour, and high metallic lustre: it is crystalline and very brittle; it tarnishes in the air, but may be preserved unchanged in pure water. Its density, in the solid state, is 5·7 to 5·9. When heated, it volatilises without fusion, and if air be present, oxidises to arsenious oxide. Its vapour-density, compared with that of hydrogen, is 150, which is twice its atomic weight, so that its molecule in the gaseous state, like that of phosphorus, occupies only half the volume of a molecule of hydrogen (p. 250). The vapour has the odour of garlic.

Arsenic combines with metals in the same manner as sulphur and phosphorus, which it resembles, especially the latter, in many respects: indeed, it is often regarded as a metalloïd.

Arsenic, like nitrogen, behaves in most respects as a triad element, not being capable of uniting with more than three atoms of any one monad element. Thus it forms the compounds AsH_3, $AsCl_3$, $AsBr_3$, &c., but no compound analogous to the pentachloride of phosphorus or antimony. But just as ammonia, NH_3, can take up the elements of hydrochloric acid to form sal-ammoniac, NH_4Cl, in which nitrogen appears quinquivalent, so likewise can arsenetted hydrogen or arsine, AsH_3, unite with the chlorides, bromides, &c., of the radicles, methyl, ethyl, &c., to form salts in which the arsenic appears to be quinquivalent, *e.g.*:

Arsenethylium bromide, .	$AsH_3(C_2H_5)Br$,
Arsenmethylium chloride, .	$AsH_3(CH_3)Cl$.

---

* Blue or Bengal light:

Dry potassium nitrate, ...	6 parts.
Sulphur, ...	2 ,,
Antimony trisulphide, ...	1 part.

All in fine powder, and intimately mixed.

In like manner, arsentrimethyl, $As(CH_3)_3$, unites with the chlorides of methyl and ethyl, forming the compounds $As(CH_3)_4Cl$ and $As(CH_3)_3(C_2H_5)Cl$.

Arsenic likewise forms two oxides, viz., arsenious oxide, As_2O_3, and arsenic oxide, As_2O_5, with corresponding acids and salts, analogous to the phosphorous and phosphoric compounds: the arsenates, in particular, are isomorphous with the orthophosphates, and resemble them closely in many other respects.

Arsenious Chloride, $AsCl_3$.—This, the only known chloride of arsenic, is produced, with emission of heat and light, when powdered arsenic is thrown into chlorine gas. It is prepared by distilling a mixture of 1 part of metallic arsenic and 6 parts of corrosive sublimate, and by distilling arsenious oxide with strong hydrochloric acid, or with a mixture of common salt and sulphuric acid. It is a colourless, volatile, highly poisonous liquid, decomposed by water into arsenious and hydrochloric acids. *Arsenious iodide*, AsI_3, is formed by heating metallic arsenic with iodine : it is a deep red crystalline substance, capable of sublimation. The corresponding *bromide* and *fluoride* are both liquid.

Hydrides.—Arsenic forms two hydrides, containing 2 and 3 atoms of hydrogen combined with 1 atom of arsenic.

The *trihydride, Arsenious hydride, Arsenetted hydrogen* or *Arsine*, AsH_3, analogous in composition to ammonia, phosphine, and stibine, is obtained pure by the action of strong hydrochloric acid on an alloy of equal parts of zinc and arsenic, and is produced in greater or lesser proportion whenever hydrogen is set free in contact with arsenious acid. Arsenetted hydrogen is a colourless gas, of specific gravity 2·695, slightly soluble in water, and having the smell of garlic. It burns, when kindled, with a blue flame, generating arsenious acid. It is also decomposed by transmission through a red-hot tube. Many metallic solutions are precipitated by this substance. When inhaled, it is exceedingly poisonous, even in very minute quantity.

The *dihydride* AsH_2, or rather $As_2H_4 = \begin{array}{c} AsH_2 \\ | \\ AsH_2 \end{array}$, is produced by passing an electric current through water, the negative pole being formed of metallic arsenic; also when potassium or sodium arsenide is dissolved in water. It is a brown powder, which gives off hydrogen when heated in a close vessel, and burns when heated in the air. It is analogous in composition to arsendimethyl or cacodyl, $As_2(CH_3)_4$.

Arsenious Oxide, Acid, and Salts.—*Arsenious oxide*, As_2O_3, also called *white oxide of arsenic*, is produced in the manner already mentioned. It is commonly met with in the form of a heavy, white, glassy-looking substance, with smooth conchoïdal fracture, having evidently undergone fusion. When freshly prepared it is often transparent, but by keeping becomes opaque, at the same time slightly diminishing in density, and acquiring a greater degree of solubility in water. 100 parts of that liquid dissolve at 100° about 11·5 parts of the opaque variety: the larger portion separates, however, on cooling, leaving about 3 parts dissolved: the solution, which contains *arsenious acid*, feebly reddens litmus. Cold water, agitated with powdered arsenious oxide, takes up a still smaller quantity. Alkalis dissolve this substance freely, forming arsenites; compounds with ammonia, baryta, strontia, lime, magnesia, and manganous oxide also have been formed: the silver salt is a beautiful lemon-yellow precipitate. The arsenites are, however, very unstable. Those which have the composition M_3AsO_3, or $3M_2O.As_2O_3$, are regarded as normal salts; there are also arsenites containing $M_4As_2O_5$, or $2M_2O.As_2O_3$, and $MAsO_2$, or $M_2O.As_2O_3$, besides acid salts. Arsenious oxide is easily soluble in hot hydrochloric acid. Its vapour is colourless and inodorous, and it crystallises on solidifying in brilliant transparent octohedrons. The oxide or acid itself has a feeble sweetish and astringent taste, and is a most fearful poison.

Arsenic Oxide, Acid and Salts.—When powdered arsenious oxide is dissolved in hot hydrochloric acid, and oxidised by the addition of nitric acid, the latter being added as long as red vapours are produced, the whole then cautiously evaporated to complete dryness, and the residue heated to low redness, arsenic oxide, As_2O_5, remains in the form of a white anhydrous mass which has no action upon litmus. When strongly heated, it is resolved into arsenious oxide and free oxygen. In water it dissolves slowly but completely, giving a highly acid solution, which, on being evaporated to a syrupy consistence, deposits, after a time, hydrated crystals of arsenic acid, containing $2H_3AsO_4.H_2O$, or $3H_2O.As_2O_5+aq$. These crystals, when heated to 100°, give off their water of crystallisation and leave *trihydric arsenate*, H_3AsO_4, or $3H_2O.As_2O_5$; at 140°–160°, *dihydric arsenate*, $H_4As_2O_7$, or $2H_2O.As_2O_5$, is left; and at 260°, *monohydric arsenate*, $HAsO_3$, or $H_2O.As_2O_5$. The aqueous solutions of the three hydrates and of the anhydrous oxide exhibit exactly the same characters, and all contain trihydric arsenate, the other hydrates being immediately converted into that compound when dissolved in water; in this respect the hydrates of arsenic oxide differ essentially from those of phosphoric oxide (p. 238).

Arsenic acid is a very powerful acid, forming salts isomorphous with the corresponding phosphates: it is also tribasic. A *sodium arsenate*, $Na_2HAsO_4.12H_2O$, undistinguishable in appearance from common sodium phosphate, may be prepared by adding the carbonate to a solution of arsenic acid, until an alkaline reaction is apparent, and then evaporating. This salt also crystallises with 7 molecules of water. Another arsenate, $Na_3AsO_4.12H_2O$, is produced when sodium carbonate in excess is fused with arsenic acid, or when the preceding salt is mixed with caustic soda. A third, $NaH_2AsO_4.H_2O$, is made by substituting an excess of arsenic acid for the solution of alkali. The alkaline arsenates which contain basic water lose the latter at a red heat, but, unlike the phosphates, recover it when again dissolved. The arsenates of the alkalis are soluble in water: those of the earths and other metallic oxides are insoluble, but are dissolved by acids. The precipitate with silver nitrate is highly characteristic of arsenic acid; it is reddish-brown.

Sulphides.—Two sulphides of arsenic are known. The *disulphide*, As_2S_2, occurs native as *Realgar*. It is formed artificially by heating arsenic acid with the proper proportion of sulphur. It is an orange-red, fusible, and volatile substance, employed in painting, and by the pyrotechnist in making *white fire*. The *trisulphide* or *arsenious sulphide*, As_2S_3, also occurs native as *Orpiment*, and is prepared artificially by fusing arsenic with the appropriate quantity of sulphur, or by precipitating a solution of arsenious acid with hydrogen sulphide. It is a golden-yellow, crystalline substance, fusible, and volatile by heat. A cold solution of arsenic acid is not immediately precipitated by hydrogen sulphide, but after some hours the solution, saturated with hydrogen sulphide, yields a light yellow deposit of sulphur, the arsenic acid being reduced to arsenious acid, which is then gradually converted into lemon-yellow arsenious sulphide. In boiling solutions the precipitation takes place immediately. The mixture of sulphur and trisulphide thus produced, was formerly regarded as a pentasulphide analogous to arsenic acid.

The disulphide and trisulphide of arsenic are sulphur-acids, uniting with other metallic sulphides to form sulphur salts. Those of the disulphide are called hyposulpharsenites; they are but little known. The salts of arsenious sulphide are called sulpharsenites. Their composition may be represented by that of the potassium salts, viz., $KAsS_2$, or $K_2S.As_2S_3$; $K_4As_2S_5$, or $2K_2S.As_2S_3$; and K_3AsS_3, or $3K_2S.As_2S_3$. Of these the bibasic salts are the most common. The sulpharsenites of the alkali metals and alkaline earth metals are soluble in water, and may be prepared by digesting arsenious sulphide in the solutions of the corresponding hydrates or sulphydrates; the rest are insoluble, and are obtained by precipitation. Sulphur salts, called sulpharsenates, analogous in composition to the arsenates, are produced, in like manner, by digesting the mixture of sulphur and arsenious sulphide precipitated, as above mentioned, from arsenic acid, in solutions of alkaline hydrates or sulphydrates; also by passing gaseous hydrogen sulphide through solutions of arsenates. There are three sulpharsenates of potassium, containing $KAsS_3$, or $K_2S.As_2S_5$; $K_4As_2S_7$, or $2K_2S.As_2S_5$; and K_3AsS_4, or $3K_2S.As_2S_5$. The sulpharsenates of the alkali metals and alkaline earth metals are soluble in water; the rest are insoluble and are obtained by precipitation.

Arsenious acid is distinguished by characters which cannot be misunderstood.

Silver nitrate, mixed with a solution of arsenious acid in water, occasions no precipitate, or merely a faint cloud: but if a little fixed alkali, or a drop of ammonia, be added, a yellow precipitate of silver arsenite immediately falls. The precipitate is exceedingly soluble in excess of ammonia; that liquid must, therefore, be added with great caution; it is likewise very soluble in nitric acid.

Cupric sulphate gives no precipitate with solution of arsenious acid, until the addition has been made of a little alkali, when a brilliant yellow-green precipitate (Scheele's green) falls, which also is very soluble in excess of ammonia.

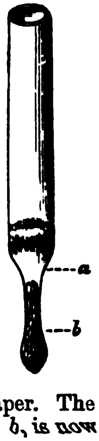
Hydrogen sulphide, passed into a solution of arsenious acid, to which a few drops of hydrochloric or sulphuric acid have been added, throws down a copious bright yellow precipitate of orpiment, which is easily dissolved by ammonia, and reprecipitated by acids.

Solid arsenious oxide, heated by the blowpipe in a narrow glass tube with small fragments of dry charcoal, affords a sublimate of metallic arsenic in the shape of a brilliant steel-grey metallic ring. A portion of this, detached by the point of a knife, and heated in a second glass tube, with access of air, yields, in its turn, a sublimate of colourless, transparent, octohedral crystals of arsenious oxide.

All these experiments, which *jointly* give demonstrative proof of the presence of the substance in question, may be performed with perfect precision and certainty upon exceedingly small quantities of material.

The detection of arsenious acid in complex mixtures, containing organic matter and common salt, as beer, gruel, soup, &c., or the fluid contents of the stomach in cases of poisoning, is a far more difficult problem, but one which is, unfortunately, often required to be solved. These organic matters interfere completely with the liquid tests, and render their indications worthless. Sometimes the difficulty may be eluded by a diligent search in the suspected liquid, and in the vessel containing it, for fragments or powder of solid arsenious oxide, which, from its small degree of solubility, often escape solution, and from the high density of the substance, may be found at the bottom of the vessels in which the fluids are contained. If anything of the kind be found, it may be washed by decantation with a little cold water, dried, and then reduced with charcoal. For the latter purpose, a small glass tube is taken, having the figure represented in the margin; white German glass, free from lead, is to be preferred. The arsenious oxide, or what is suspected to be such, is dropped to the bottom, and covered with splinters or little fragments of charcoal, the tube being filled to the shoulder. The whole is gently heated, to expel any moisture that may be present in the charcoal, and the deposited water wiped from the interior of the tube with bibulous paper. The narrow part of the tube containing the charcoal, from *a* to *b*, is now

Fig. 152.



[illegible], by chasing it up and down by
A little water may afterwards be int
by which arsenious oxide will be
the tests of silver nitrate and amm
monia, and hydrogen sulphide, may

When the search for solid arsenio
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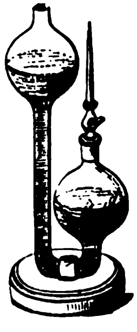
a little caustic potash or acetic aci
object. The following is an outline
found successful in a variety of cases i
of arsenious acid had been purposely ac
Oil of vitriol, itself perfectly free fro
suspected liquid, in the proportion of
pint, having been previously diluted
whole is boiled in a flask for half a
separation of solid and liquid matter
converts any starch that may be presen
completely coagulates albuminous subst
of milk, and brings the whole in a ve
which filtration is both easy and rapid.
tion, when cold, a current of hydrogen
the liquid is warmed, to facilitate the
sulphide, which falls in combination
organic matter, which often communi
This is collected upon a small filter, an
ferred

described, with similar precautions; a ring of reduced arsenic is obtained, which may be oxidised to arsenious oxide, and further examined. The black flux is a mixture of potassium carbonate and charcoal, obtained by calcining cream of tartar in a close crucible; the alkali transforms the sulphide into arsenious acid, the charcoal subsequently effecting the deoxidation. A mixture of anhydrous sodium carbonate and charcoal may be substituted with advantage for the common black flux, as it is less hygroscopic.

Other methods of proceeding, different in principle from the foregoing, are also employed, as that of the late Mr. Marsh, which is exceedingly delicate. The suspected liquid is acidulated with sulphuric acid, and placed in contact with metallic zinc; the hydrogen reduces the arsenious acid and combines with the arsenic, if any be present. The gas is burned at a jet, and a piece of glass or porcelain held in the flame, when any admixture of arsenetted hydrogen is at once known by the production of a brilliant black metallic spot of reduced arsenic on the porcelain; or the gas is passed through a glass tube heated at one or two places to redness, whereby the arsenetted hydrogen is decomposed, a ring of metallic arsenic appearing behind the heated portion of the tube.

It has been observed (page 447) that antimonetted hydrogen gives a similar result. In order to distinguish the two substances, the gas may be passed into a solution of silver nitrate. Both gases give rise to a black precipitate, which, in the case of antimonetted hydrogen, consists of silver antimonide, Ag_3Sb, whilst in the case of arsenetted hydrogen, it is pure silver, the arsenic being then converted into arsenious acid, which combines with a portion of silver oxide. The silver arsenite remains dissolved in the nitric acid which is liberated by the precipitation of the silver, and may be thrown down with its characteristic yellow colour by adding ammonia to the liquid filtered off from the black precipitate. The black silver antimonide, when carefully washed, and subsequently boiled with a solution of tartaric acid, yields a solution containing antimony only, from which hydrogen sulphide separates the characteristic orange-yellow precipitate of antimonious sulphide.

Fig. 153.



A convenient form of Marsh's instrument is that shown in fig. 153: it consists of a bent tube, having two bulbs blown upon it, fitted with a stop-cock and narrow jet. Slips of zinc are put into the lower bulb, which is afterwards filled with the liquid to be examined. On replacing the stop-cock, closed, the gas collects and forces the liquid into the upper bulb, which then acts by its hydrostatic pressure, and expels the gas through the jet so soon as the stop-cock is opened. It must be borne in mind that both common zinc and sulphuric acid often contain traces of arsenic. Professor

Bloxam* has proposed an important modification of Marsh's process for the detection of arsenic and antimony in organic substances, which is based on the behaviour of solutions of these metals under the influence of the electric current. Antimony is deposited in the metallic state, without any disengagement of antimonetted hydrogen, while arsenic is evolved as arsenetted hydrogen, which may be recognised by the characters already indicated.

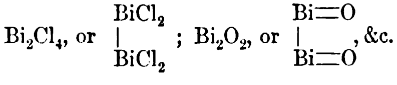
A slip of copper-foil boiled in the poisoned liquid, previously acidulated with hydrochloric acid, withdraws the arsenic, and becomes covered with a white alloy. By heating the metal in a glass tube, the arsenic is expelled, and oxidised to arsenious acid. This is called Reincsh's test.

BISMUTH.

Atomic weight, 210. Symbol, Bi.

BISMUTH is found chiefly in the metallic state, disseminated through various rocks, from which it is separated by simple exposure to heat. The metal is highly crystalline and very brittle: it has a reddish-white colour, and a density of 9·9. Crystals of great beauty may be obtained by slowly cooling a considerable mass of this substance until solidification has commenced, then piercing the crust, and pouring out the fluid residue. Bismuth melts at about 260°, and volatilises at a high temperature. It is remarkable as being the most diamagnetic of all known bodies. It is little oxidised by the air, but burns with a bluish flame when strongly heated. Nitric acid somewhat diluted dissolves it freely.

Bismuth forms three classes of compounds, in which it is bi-, tri-, and quinquivalent respectively. The tri-compounds are the most stable and the most numerous. The only known compounds in which bismuth is quinquivalent are indeed the pentoxide, Bi_2O_5, together with the corresponding acid and metallic salts. Nevertheless, bismuth is regarded as a pentad, on account of the analogy of its compounds with those of antimony. Several bismuth compounds are known in which the metal is apparently bivalent, but really trivalent, as :



$$Bi_2Cl_4, \text{ or } \begin{array}{c} BiCl_2 \\ | \\ BiCl_2 \end{array} ; \; Bi_2O_2, \text{ or } \begin{array}{c} Bi{=}O \\ | \\ Bi{=}O \end{array}, \&c.$$

Chlorides.—The *trichloride*, or *Bismuthous chloride*, is formed when bismuth is heated in a current of chlorine gas, and passes over as a white, easily fusible substance, which readily attracts moisture from the air, and is converted into a crystallised hydrate. The same substance is produced when bismuth is dissolved in nitromuriatic acid, and the solution evaporated. Bismuthous chloride dissolves in water containing hydrochloric acid, but is decomposed by pure water, yielding a white precipitate of oxychloride:

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* Journal of the Chemical Society, xiii. 338.

$$BiCl_3 + H_2O = BiClO + 2HCl.$$

The *dichloride*, Bi_2Cl_4, produced by heating the trichloride with metallic bismuth, is a brown, crystalline, easily fusible mass, decomposed by water. At a high temperature it is resolved into the trichloride and metallic bismuth.

Oxides.—The *trioxide*, or *Bismuthous oxide*, is a straw-yellow powder, obtained by gently igniting the neutral or basic nitrate. It is fusible at a high temperature, and in that state acts towards siliceous matter as a powerful flux.

The *hydrate*, $BiHO_2$ or $Bi_2O_3.H_2O$, is obtained as a white precipitate when a solution of the nitrate is decomposed by an alkali. Both the hydrate and the anhydrous oxide dissolve in the stronger acids, forming the bismuthous salts, which have the composition BiR_3, where R denotes an acid radicle, *e.g.*, $BiCl_3$, $Bi(NO_3)_3$, $Bi_2(SO_4)_3$ Many of these salts crystallise well, but cannot exist in solution unless an excess of acid is present. On diluting the solutions with water, a basic salt is precipitated, and an acid salt remains in solution.

The *normal nitrate*, $Bi(NO_3)_3.5H_2O$, or $Bi_2O_3.3N_2O_5.10H_2O$, forms large transparent colourless crystals, which are decomposed by water in the manner just mentioned, yielding an acid solution containing a little bismuth, and a brilliant white crystalline powder, which varies to a certain extent in composition according to the temperature and the quantity of water employed, but frequently consists of a basic nitrate, $Bi_2O_3.N_2O_5.2H_2O$, or $Bi(NO_3)_3.Bi_2O_3.3H_2O$. A solution of bismuth nitrate, free from any great excess of acid, poured into a large quantity of cold water, yields an insoluble basic nitrate, very similar in appearance to the above, but containing rather a larger proportion of bismuth oxide. This basic nitrate was once extensively employed as a cosmetic, but it is said to injure the skin, rendering it yellow and leather-like. It is used in medicine.

Bismuth pentoxide, or *Bismuthic oxide*, Bi_2O_5.—When bismuth trioxide is suspended in a strong solution of potash, and chlorine passed through the liquid, decomposition of water ensues, hydrochloric acid being formed, and the trioxide being converted into the pentoxide. To separate any trioxide that may have escaped oxidation, the powder is treated with dilute nitric acid, when the bismuthic oxide is left as a reddish powder, which is insoluble in water. This substance combines with bases, but the compounds are not very well known. According to Arppe, there is an acid potassium bismuthate containing Bi_2KHO_6, or $2Bi_2O_5 . \left\{ \begin{matrix} K_2O \\ H_2O \end{matrix} \right.$. The pentoxide when heated loses oxygen, an intermediate oxide, Bi_2O_4, being formed, which may be considered as *bismuthous bismuthate*, $2Bi_2O_4 = Bi_2O_3.Bi_2O_5$.

Bismuth is sufficiently characterised by the decomposition of its nitrate and chloride by water, and by the black precipitate of bismuth sulphide, insoluble in ammonium sulphide, which its solutions yield when exposed to the action of hydrogen sulphide.

A mixture of 8 parts of bismuth, 5 parts of lead, and 3 of tin, is known under the name of *fusible metal*, and is employed in taking impressions from dies and for other purposes: it melts below 100°.

Bismuth is used, in conjunction with antimony, in the construction of thermo-electric piles, these two metals forming the opposite extremes of the thermo-electric series.

VANADIUM.

Atomic weight, 51·2. Symbol, V.

VANADIUM is found, in small quantity, in some iron ores, also as *vanadate of lead*. It has likewise been discovered in the iron slag of Staffordshire, and recently, by Roscoe,* in larger quantity in the copper-bearing beds at Alderley Edge and Mottram St Andrews, in Cheshire. Metallic vanadium is obtained by prolonged ignition of the dichloride in pure dry hydrogen, as a greyish white powder, appearing under the microscope as a crystalline mass, with a strong silver-white lustre. It is non-volatile, decomposes water at 100°, does not tarnish in the air, burns with brilliant scintillations when thrown into a flame; burns vividly when quickly heated in oxygen, forming the pentoxide; is insoluble in hydrochloric acid; dissolves slowly in hydrofluoric acid with evolution of hydrogen, rapidly in nitric acid, forming a blue solution. In a current of chlorine it takes fire, and is converted into the tetrachloride.

Vanadium was, till lately, regarded as a hexad metal, analogous to tungsten and molybdenum; but Roscoe has shown that it is a pentad, belonging to the phosphorus and arsenic group. This conclusion is based upon the composition of the oxides and oxychlorides; and on the isomorphism of the vanadates with the phosphates.

Vanadium Oxides.—Vanadium forms five oxides, represented by the formulæ, V_2O, V_2O_2, V_2O_3, V_2O_4, V_2O_5, analogous, therefore, to the oxides of nitrogen.

The *monoxide*, V_2O, is formed by prolonged exposure of metallic vanadium to the air at ordinary temperatures, more quickly at a dull red heat. It is a brown substance, which, when heated in the air, is gradually converted into the higher oxides.

The *dioxide*, V_2O_2, which was regarded by Berzelius as metallic vanadium, is obtained by reducing either of the higher oxides with potassium, or by passing the vapour of vanadium oxytrichloride, ($VOCl_3$), mixed with excess of hydrogen, through a combustion tube containing red-hot charcoal. As obtained by the second process, it forms a light-grey glittering powder, or a metallically lustrous crystalline crust, having a specific gravity of 3·64, brittle, very difficult to fuse, and a conductor of electricity. When heated to redness in the air, it takes fire and burns to black oxide. It is insoluble in sulphuric, hydrochloric, and hydrofluoric acid, but dissolves easily in nitromuriatic acid, forming a dark-blue liquid.

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* Proceedings of the Royal Society, xvi. 223.

The dioxide may be prepared in solution by the action of nascent hydrogen (evolved by metallic zinc, cadmium, or sodium-amalgam), on a solution of vanadic acid in sulphuric acid. After passing through all shades of blue and green, the liquid acquires a permanent lavender tint, and then contains the vanadium in solution as dioxide, or as hypovanadious salt. This compound absorbs oxygen more rapidly than any other known agent, and bleaches indigo and other vegetable colours as quickly as chlorine.

Vanadium dioxide may be regarded as entering into many vanadium compounds, as a bivalent radicle (just like uranyl in the uranic compounds), and may therefore be called *vanadyl*.

Vanadium trioxide, V_2O_3, or *Vanadyl monoxide*, $(V_2O_2)''O$, is obtained by igniting the pentoxide in hydrogen gas, or in a crucible lined with charcoal. It is a black powder, with an almost metallic lustre, and infusible; by pressure it may be united into a coherent mass which conducts electricity. When exposed warm to the air, it glows, absorbs oxygen, and is converted into pentoxide. At ordinary temperatures, it slowly absorbs oxygen, and is converted into tetroxide. By ignition in chlorine gas it is converted into vanadyl trichloride and vanadium pentoxide. It is insoluble in acids, but may be obtained in solution by the reducing action of nascent hydrogen (evolved from metallic magnesium) on a solution of vanadic acid in sulphuric acid.

Vanadium tetroxide, *Hypovanadic oxide*, or *Vanadyl dioxide*, $V_2O_4 = (V_2O_2)O_2$.—This oxide is produced, either by oxidation of the dioxide or trioxide, or by partial reduction of the pentoxide; also by heating hypovanadic chloride, $V_2O_4Cl_2$, to redness in an atmosphere of carbon dioxide.[*] By allowing the trioxide to absorb oxygen at ordinary temperatures, the tetroxide is obtained in blue shining crystals. It dissolves in acids, the more easily in proportion as it has been less strongly ignited, forming solutions of hypovanadic salts, which have a bright blue colour. The same solutions are produced by the action of moderate reducing agents, such as sulphurous, sulphydric, or oxalic acid, upon vanadic acid in solution; also by passing air through acid solutions of the dioxide till a permanent blue colour is attained. With the *hydrates* and *normal carbonates of the fixed alkalis*, they form a greyish-white precipitate of hydrated oxide, $V_2O_4.H_2O$, which dissolves in a moderate excess of the reagent, but is reprecipitated by a large excess in the form of a vanadite of the alkali metal.

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[*] J. K. Crow, Chem. Soc. Jour., 1876, ii

Ammonia in excess produces a brown precipitate, soluble in pure water, but insoluble in water containing ammonia.—*Ammonium sulphide* forms a black-brown precipitate, soluble in excess.—*Tincture of galls* forms a finely divided black precipitate, which gives to the liquid the appearance of ink.

Hypovanadic trisulphate, $V_2O_4.3SO_3+6H_2O$, is obtained as a blue deliquescent crystalline powder by dissolving vanadic oxide in strong sulphuric acid and reducing the solution with sulphurous acid. A salt of similar character, containing $4H_2O$, is obtained by precipitating the concentrated solution with strong sulphuric acid. A *disulphate*, $V_2O_4.2SO_3+7H_2O$, is obtained as a light-blue crystalline powder, when the pure trisulphate, or the residue left on evaporating a solution of the tetroxide in sulphuric acid, is treated with absolute alcohol (Crow). Berzelius by similar means obtained a disulphate with $4H_2O$.

Vanadium tetroxide also unites with the more basic metallic oxides, forming salts called hypovanadates, all of which are insoluble, except those of the alkali-metals. The solutions of the alkaline hypovanadates are brown, but when treated with *hydrogen sulphide* they acquire a splendid red-purple colour, arising from the formation of a sulphur salt.—*Acids* colour them blue, by forming a double hypovanadic salt; *tincture of galls* colours them blackish-blue. The insoluble hypovanadates, when moistened or covered with water, become green, and are converted into vanadates.

Crow has obtained the following hypovanadates by treating hypovanadic chloride with the corresponding bases :—

Potassium salt, . .	$K_2O.2V_2O$	$+ 7H_2O$
Sodium salt, . . .	$Na_2O.2V_2O_4$	$+ 7H_2O$
Ammonium salt, . .	$(NH_4)_2O.2V_2O_4$	$+ 3H_2O$
Barium salt, . . .	$BaO.2V_2O_4$	$+ 5H_2O$.

The *lead salt*, $PbO.V_2O_4$, is formed, together with potassium acetate and free acetic acid, by precipitating a solution of lead acetate with potassium hypovanadate :

$$K_2O.2V_2O_4 + 2Pb(C_2H_3O_2)_2 + H_2O = 2(PbO.V_2O_4) + 2KC_2H_3O_2 + 2C_2H_4O_2 .$$

The *silver salt*, $Ag_2O.V_2O_4$, is formed by a precisely similar reaction from potassium hypovanadate and silver nitrate.

Vanadium pentoxide, *Vanadic oxide*, or *Vanadyl trioxide*, $V_2O_5 = (V_2O_2)O_3$.—This is the highest oxide of vanadium. It may be prepared from native lead vanadate. This mineral is dissolved in nitric acid, and the lead and arsenic are precipitated by hydrogen sulphide, which at the same time reduces the vanadium pentoxide to tetroxide. The blue filtered solution is then evaporated to dryness, and the residue digested in ammonia, which dissolves out the vanadic oxide reproduced during evaporation. In this solution a lump of sal-ammoniac is put; as that salt dissolves, ammonium vanadate subsides as a white powder, being scarcely soluble in a saturated solution of ammonium chloride. By exposure to a temperature below redness in an open crucible, the ammonia is expelled, and vanadic oxide left. By a similar process, Roscoe has prepared vanadic oxide from a lime precipitate containing 2 per cent. of vanadium, obtained in working up a poor cobalt ore from Mottram in Cheshire.

Vanadium pentoxide has a reddish-yellow colour, and dissolves in 1000 parts of water, forming a light yellow solution. It dissolves also in stronger acids, forming red or yellow solutions, some of which yield crystalline compounds (vanadic salts) by spontaneous evaporation. It unites, however, with bases more readily than with acids, forming salts called vanadates. When fused with alkaline carbonates, it eliminates 3 molecules of carbon dioxide, forming *orthovanadates* analogous to the orthophosphates; thus:

$$3(Na_2O.CO_2) + V_2O_5 = 3Na_2O.V_2O_5 + 3CO_2.$$

It also forms *metavanadates* and *pyrovanadates* analogous to the meta- and pyro-phosphates, and two series of acid *vanadates* or *anhydrovanadates*, viz.:

Lead orthovanadate, .	$Pb_3(VO_4)_2$	or $3PbO.V_2O_5$
Barium pyrovanadate, .	$Ba_2V_2O_7$	or $2BaO.V_2O_5$
Strontium metavanadate,	$Sr(VO_3)_2$	or $SrO.V_2O_5$
Strontium divanadate,	$Sr(VO_3)_2.V_2O_5$	or $SrO.2V_2O_5$
Strontium trivanadate,	$Sr(VO_3)_2.2V_2O_5$	or $SrO.3V_2O_5$.

Lead metavanadate occurs native as *dechenite*; the orthovanadate also, combined with lead chloride, as *vanadinite* or *vanadite*, $PbCl_2.3Pb_3(VO_4)_2$, the mineral in which vanadium was first discovered. *Descloizite* is a diplumbic vanadate, $Pb_2V_2O_7$, or $2PbO.V_2O_5$, analogous in composition to a pyrophosphate.

The metavanadates are mostly yellow; some of them, however, especially those of the alkaline earth metals, and of zinc, cadmium, and lead, are converted by warming—either in the solid state, or under water, or in aqueous solution, especially in presence of a free alkali or alkaline carbonate—into isomeric colourless salts. The same transformation takes place also, though more slowly, at ordinary temperatures. The metavanadates of alkali-metal are colourless. The acid vanadates are yellow, or yellowish red, both in the solid state and in solution: hence the solution of a neutral vanadate becomes yellowish-red on addition of an acid. The metavanadates of ammonium, the alkali-metals, barium, and lead, are but sparingly soluble in water; the other metavanadates are more soluble. The alkaline vanadates are more soluble in pure water than in water containing free alkali or salt: hence they are precipitated from their solutions by addition of alkali in excess, or of salts. The vanadates are insoluble in alcohol. The aqueous solutions of vanadates form yellow precipitates with *antimony, copper, lead,* and *mercury* salts; with *tincture of galls* they form a deep black liquid, which has been proposed for use as vanadium ink.

Hydrogen sulphide reduces them to hypovanadates, changing the colour from red or yellow to blue, and forming a precipitate of sulphur.

Ammonium sulphide colours the solutions brown-red, and, on adding an acid, a light-brown precipitate is formed, consisting of vanadic sulphide mixed with sulphur, the liquid at the same time turning blue. *Hydrochloric acid* decomposes the vanadates, with evolution of chlorine and formation of vanadium tetroxide.

Vanadium Chlorides.—Three of these compounds have been obtained, viz.: VCl_2, VCl_3 and VCl_4.

The *tetrachloride*, VCl_4 is formed when metallic vanadium or the mononitride is heated in a current of chlorine, or when the vapour of the oxytrichloride, $VOCl_3$, mixed with chlorine, is passed several times over red-hot charcoal. It is a dark yellowish-brown liquid, having a specific gravity of 1·8384 at 0°, boiling at 154°, not solidifying at 18°. Its vapour-density referred to hydrogen is 96·6, which is half the molecular weight, $\left(=\frac{51·5 + 4 \times 35·5}{2}\right)$, showing that the molecule VCl_4 exhibits the normal condensation to 2 volumes of vapour. The tetrachloride is quickly decomposed by water, forming a blue solution of vanadious acid. It does not take up bromine or an additional quantity of chlorine when heated therewith in sealed tubes: hence it appears that vanadium does not readily form pentad compounds with the monatomic chlorous elements.

The *trichloride*, VCl_3, obtained by decomposition of the tetrachloride, slowly at ordinary temperatures, quickly at the boiling heat, crystallises in peach-blossom-coloured shining plates resembling chromic chloride. It is slowly decomposed by water, forming a green solution of hypovanadic acid.

The *dichloride*, VCl_2, obtained by passing the vapour of the tetrachloride mixed with hydrogen through a red-hot tube, crystallises in green micaceous plates, which are decomposed by water, forming a violet solution of hypovanadious acid.

Vanadium Oxychlorides, or **Vanadyl Chlorides.**—Four of these compounds are known, viz.,: $VOCl_3$, $VOCl_2$, $VOCl$, and V_2O_2Cl.

The *oxytrichloride* $VOCl_3$, (formerly regarded as vanadium trichloride), is prepared:

(1) By the action of chlorine on the trioxide:

$$3V_2O_3 + Cl_{12} = V_2O_5 + 4VOCl_3\,.$$

(2) By burning the dioxide in chlorine gas, or by passing that gas over an ignited mixture of the trioxide, tetroxide, or pentoxide, and condensing the vapours in a cooled U-tube.

Vanadium oxytrichloride, or vanadyl trichloride, is a golden-yellow liquid, of specific gravity 1·841 at 14·5°. Boiling-point, 127°. Vapour-density, by experiment, 6·108 ; by calculation, 6·119. When exposed to the air, it emits cinnabar-coloured vapours, being resolved by the moisture of the air into hydrochloric and vanadic acids. It oxidises magnesium and sodium. Its vapour, passed over perfectly pure carbon at a red heat, yields carbon dioxide ; and when passed, together with hydrogen, through a red-hot tube, yields vanadium trioxide. These reactions show that the compound contains oxygen.

The other oxychlorides of vanadium are solid bodies obtained by partial reduction of the oxytrichloride with zinc or hydrogen.

The second, $VOCl_2$ or $V_2O_2Cl_4$ (hypovanadic chloride), is also produced by dissolving the pentoxide, with aid of heat, in hydrochloric acid, and reducing the green solution with sulphurous acid. The resulting blue liquid leaves, on evaporation over the water bath, a brown deliquescent residue which yields a blue solution with water (Crow).

The *tribromide*, VBr_3, and the *oxybromides*, $VOBr_3$ and $VOBr_2$, have also been obtained. The first is a greyish-black amorphous solid ; the second a dark-red liquid ; the third a yellowish-brown deliquescent solid.

Vanadium Sulphides.—Two of these compounds are known, analogous to the tetroxide and pentoxide; both are sulphur-acids. The *tetrasulphide*, or *Vanadious sulphide*, V_2S_4, is a black substance formed by heating the tetroxide to redness in a stream of hydrogen sulphide ; also as a hydrate by dissolving a vanadious salt in excess of an alkaline monosulphide, and precipitating with hydrochloric acid. The *pentasulphide*, or *Vanadic sulphide*, V_2S_5, is formed in like manner by precipitation from an alkaline vanadate.

Vanadium Nitrides.—The *mononitride*, VN, is formed by heating the compound of vanadium oxytrichloride with ammonium chloride to whiteness in a current of ammonia gas. It is a greenish-white powder unalterable in the air. The *dinitride*, VN_2 or V_2N_4, is obtained by exposing the same double salt in ammonia gas to a moderate heat. It is a black powder strongly acted upon by nitric acid.

All vanadium compounds heated with borax or phosphorus-salt in the outer blowpipe flame produce a clear bead, which is colourless if the quantity of vanadium is small, yellow when it is large ; in the inner flame the bead acquires a beautiful green colour.

Vanadic and chromic acids are the only acids whose solutions are red ; they are distinguished from one another by the vanadic acid becoming blue, and the chromic acid green, by deoxidation.

When a solution of vanadic acid, or an acidulated solution of an alkaline vanadate, is shaken up with ether containing hydrogen dioxide, the aqueous solution acquires a red colour, like that of ferric acetate, while the ether remains colourless. This reaction will serve to detect the presence of 1 part of vanadic acid in 40,000 parts of liquid. The other reactions of vanadium in solution have already been described.

TANTALUM.

Atomic weight, 182. Symbol, Ta.

THIS metal was discovered, in 1803, by Ekeberg, in two Swedish minerals, tantalite and yttrotantalite. A very similar metal, *columbium*, had been discovered in the preceding year by Hatchett, in columbite from Massachusetts; and Wollaston, in 1807, on comparing the compounds of these metals, concluded that they were identical, an opinion which was for many years received as correct; but their separate identity has been completely established by the researches of H. Rose (commenced in 1846), who gave to the metal from the American and Bavarian columbites, the name *Niobium*, by which it is now universally known. More recently, Marignac has shown that nearly all tantalites and columbites contain both tantalum and niobium (or columbium), some tantalates, from Kimito, in Finland, being, however, free from niobium, and some of the Greenland columbites containing only the latter metal unmixed with tantalum. In all these minerals tantalum exists as a tantalate of iron and manganese; yttrotantalite is essentially a tantalate of yttrium, containing also uranium, calcium, iron, and other metals. Tantalum is also contained in some varieties of wolfram.

Metallic tantalum is obtained by heating the fluotantalate of potassium or sodium with metallic sodium in a well-covered iron crucible, and washing out the soluble salts with water. It is a black powder, which, when heated in the air, burns with a bright light, and is converted, though with difficulty, into tantalic oxide. It is not attacked by sulphuric, hydrochloric, nitric, or even nitromuriatic acid. It dissolves slowly in warm aqueous hydrofluoric acid, with evolution of hydrogen, and very rapidly in a mixture of hydrofluoric and nitric acids.

Tantalum, in its principal compounds, is quinquivalent, the formula of tantalic chloride being $TaCl_5$, that of tantalic fluoride, TaF_5, and that of tantalic oxide (which, in combination with bases forms the tantalates), Ta_2O_5. There is also a tantalous oxide, said to have the composition TaO_2, and a corresponding sulphide, TaS_2.

Tantalic Chloride, $TaCl_5$, is obtained, as a yellow sublimate, by igniting an intimate mixture of tantalic oxide and charcoal in a stream of chlorine gas. It begins to volatilise at 144°, and melts to a yellow liquid at 221°. The vapour-density between 350° and

440°, has been found by Deville and Troost to be 12·42 referred to air, or 178·9 referred to hydrogen: by calculation, for the normal condensation to two volumes, it is 179·75. Tantalic chloride is decomposed by water, yielding hydrochloric and tantalic acids; but the decomposition is not complete even at the boiling heat.

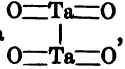
Tantalic Fluoride, TaF_5, is obtained in solution by treating tantalic hydrate with aqueous hydrofluoric acid. The solution, mixed with alkaline fluorides, forms soluble crystallisable salts, called tantalofluorides, or fluotantalates. The potassium salt, TaK_2F_7 or $TaF_5.2KF$, crystallises in monoclinic prisms, isomorphous with the corresponding fluoniobate.

Tantalic Oxide, Ta_2O_5, is produced when tantalum burns in the air, also by the action of water on tantalic chloride, and may be separated as a hydrate from the tantalates by the action of acids. It may be prepared from tantalite, which is a tantalate of iron and manganese, by fusing the finely pulverised mineral with twice its weight of potassium hydroxide, digesting the fused mass in hot water, and supersaturating the filtered solution with hydrochloric or nitric acid: hydrated tantalic oxide is then precipitated in white flocks, which may be purified by washing with water.*

Anhydrous tantalic oxide, obtained by igniting the hydrate or sulphate, is a white powder, varying in density from 7·022 to 8·264, according to the temperature to which it has been exposed. Heated in ammonia gas it yields tantalum nitride: heated with carbon bisulphide, it is converted into tantalum bisulphide. It is insoluble in all acids, and can be rendered soluble only by fusion with potassium hydrate or carbonate.

Hydrated Tantalic oxide, or *Tantalic acid,* obtained by precipitating an aqueous solution of potassium tantalate with hydrochloric acid, is a snow-white bulky powder, which dissolves in hydrochloric and hydrofluoric acids; when strongly heated, it glows and gives off water.

Tantalic oxide unites with basic metallic oxides, forming the tantalates, which are represented by the formulæ, $M_2O.Ta_2O_5$ and $4M_2O.3Ta_2O_5$, the first including the native tantalates, such as ferrous tantalate, and the second certain easily crystallisable tantalates of the alkali metals. The tantalates of the alkali-metals are soluble in water, and are formed by fusing tantalic oxide with caustic alkalis: those of the earth-metals and heavy metals are insoluble, and are formed by precipitation.

Tantalum dioxide, or *Tantalous oxide,* TaO_2, may be represented by the formula  $\begin{array}{c}O{=}Ta{=}O\\ |\\ O{=}Ta{=}O\end{array}$, in which the metal is still quinquivalent. It is produced by exposing tantalic oxide to an intense heat in a crucible lined with charcoal. It is a hard dark grey substance, which, when heated in the air, is converted into tantalic oxide.

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* For more complete methods of preparation, see Watts's Dictionary of Chemistry, vol. v. p. 665.

Hydrochloric or *sulphuric acid*, added in excess to a solution of alkaline tantalate, forms a precipitate of tantalic acid, which redissolves in excess of the hydrochloric, but not of the sulphuric acid. *Potassium ferrocyanide*, added to a very slightly acidulated solution of an alkaline tantalate, forms a yellow precipitate; the *ferricyanide*, a white precipitate. *Infusion of galls* forms a light yellow precipitate, soluble in alkalis. When tantalic chloride is dissolved in strong sulphuric acid, and then water and metallic *zinc* are added, a fine blue colour is produced, which does not turn brown, but soon disappears.

Tantalic oxide fused with microcosmic salt in either blowpipe flame forms a clear, colourless glass, which does not turn red on addition of a ferrous salt. With borax it also forms a transparent glass, which may be rendered opaque by interrupted blowing, or *flaming*.

NIOBIUM, or COLUMBIUM.

Atomic weight, 94. Symbol, Nb.

THIS metal, discovered in 1801 by Hatchett, in American columbite, exists likewise, associated with tantalum, in columbites from other sources, and in most tantalites; also, associated with yttrium, uranium, iron, and small quantities of other metals, in Siberian samarskite, uranotantalite, or yttroilmenite; also in pyrochlore, euxenite, and a variety of pitchblende from Satersdälen in Norway.

The metal, obtained in the same manner as tantalum, is a black powder, which oxidises with incandescence when heated in the air. It dissolves in hot hydrofluoric acid, with evolution of hydrogen, and, at ordinary temperatures, in a mixture of hydrofluoric and nitric acid; slowly, also, when heated with strong sulphuric acid. It is oxidised by fusion with acid potassium sulphate, and gradually converted into potassium niobate by fusion with potassium hydrate or carbonate.

Niobium is quinquivalent, and forms only one class of compounds, namely, a chloride, $NbCl_5$; oxide, Nb_2O_5; oxychloride $NbOCl_3$, &c.

Niobic Oxide, Nb_2O_5, is formed when the metal burns in the air. It is prepared from columbite, &c., by fusing the levigated mineral in a platinum crucible with 6 or 8 parts of acid potassium sulphate, removing soluble salts by boiling the fused mass with water, digesting the residue with ammonium sulphide to dissolve tin and tungsten, boiling with strong hydrochloric acid to remove iron, uranium, and other metals, and finally washing with water. Niobic oxide is thus obtained generally mixed with tantalic oxide, from which it is separated by means of hydrogen and potassium fluoride, HF.KF, which converts the tantalum into sparingly soluble potassium tantalofluoride, $2KF.TaF_5$, and the niobium into easily soluble potassium nioboxyfluoride, $2KF.NbOF_3$.aq.

Niobic oxide is also produced by decomposing niobic chloride, or oxychloride, with water: when pure it has a specific gravity of 4·4 to 4·5. It is an acid oxide, uniting with basic oxides, and forming salts called niobates, some of which occur as natural minerals: columbite, for example, being a ferro-manganous niobate. The *potassium niobates* crystallise readily, and in well-defined forms. Marignac has obtained the salts $4K_2O.3Nb_2O_5$.16aq. crystallising in monoclinic prisms; $8K_2O.7Nb_2O_5$.32aq. in pyramidal monoclinic crystals; $3K_2O.2Nb_2O_5$.13aq. in rhomboïdal prisms; and $K_2O.3Nb_2O_5$.aq. as a pulverulent precipitate, by boiling a solution of potassium nioboxyfluoride with potassium carbonate. The *sodium niobates* are crystalline powders which decompose during washing. There is also a sodium and potassium niobate, containing $Na_2O.3K_2O.3Nb_2O_5$.9 aq.

Niobic Chloride, $NbCl_5$, is obtained, together with the oxychloride, by heating an intimate mixture of niobic oxide and charcoal in a stream of chlorine gas. It is yellow, volatile, and easily fusible. Its observed vapour-density, according to Deville and Troost, is 9·6 referred to air, or 138·6 referred to hydrogen as unity: by calculation for a two-volume condensation, it is $\frac{94+5.35{\cdot}5}{2}=137{\cdot}75$. The *oxychloride*, $NbOCl_3$, is white, volatile, but not fusible: its specific gravity, referred to hydrogen, is by observation, 114·06; by calculation, $\frac{94+16+3.35{\cdot}5}{2}=109{\cdot}25$. Both these compounds are converted by water into niobic oxide.

Niobic Oxyfluoride, $NbOF_3$, is formed by dissolving niobic oxide in hydrofluoric acid. It unites with the fluorides of the more basic metals, forming salts isomorphous with the titanofluorides, stannofluorides, and tungstofluorides, 1 atom of oxygen in these salts taking the place of 2 atoms of fluorine. Marignac has obtained five potassium nioboxyfluorides, all perfectly crystallised, namely:

$2KF.NbOF_3$.aq.,	crystallising in	monoclinic plates,
$3KF.NbOF_3$	„	cuboïd forms (system undetermined),
$3KF.HF.NbOF_3$	„	monoclinic needles,
$5KF.3NbOF_3$.aq.	„	hexagonal prisms,
$4KF.3NbOF_3$.2 aq.	„	triclinic prisms.

Potassium nioboflouride, $3KF.NbF_5$, separates in shining monoclinic needles from a solution of the first of the above-mentioned nioboxyfluorides in hydrofluoric acid. Nioboxyfluorides of ammonium, sodium, zinc, and copper have also been obtained.

The isomorphism of these salts with the stannofluorides, titanofluorides, and tungstofluorides, shows clearly that the existence of isomorphism between the corresponding compounds of any two elements, must not be taken as a decided proof that those elements are of equal atomicity: for in the case now under consideration, we have isomorphous salts formed by tin and titanium, which are tetrads, niobium, which is a pentad, and tungsten, which is a hexad.

The compounds of niobium cannot easily be mistaken for those of any other metal except tantalum. The most characteristic reactions of niobates and tantalates with liquid reagents are the following:—

	Niobates.	*Tantalates.*
Hydrochloric acid . .	White precipitate, insoluble in excess.	White precipitate, soluble in excess.
Ammonium chloride .	Precipitation slow and incomplete.	Complete precipitation as acid ammonium tantalate.
Potassium ferrocyanide	Red precipitate.	Yellow precipitate.
,, ferricyanide	Bright yellow precipitate.	White precipitate.
Infusion of galls . .	Orange-red precipitate.	Light yellow precipitate.

Niobic oxide, heated with borax in the outer blowpipe flame, forms a colourless bead, which, if the oxide is in sufficient quantity, becomes opaque by interrupted blowing or flaming. In microcosmic salt it dissolves abundantly, forming a colourless bead in the outer flame, and in the inner a violet-coloured, or if the bead is saturated with the oxide, a beautiful blue bead, the colour disappearing in the outer flame.

CLASS VI.—HEXAD METALS.

CHROMIUM.

Atomic weight, 52·2. Symbol, Cr.

CHROMIUM is found in the state of oxide, in combination with iron oxide, in some abundance in the Shetland Islands, and elsewhere: as lead chromate it constitutes a very beautiful mineral, from which it was first obtained. The metal itself is prepared in a half-fused condition by mixing the oxide with half its weight of charcoal powder, enclosing the mixture in a crucible lined with charcoal, and then subjecting it to the very highest heat of a powerful furnace.

Deville has prepared metallic chromium by reducing pure chromium sesquioxide with an insufficient quantity of charcoal, in a lime crucible. Thus prepared, metallic chromium is less fusible than platinum, and as hard as corundum. It is readily acted upon by dilute hydrochloric acid, less so by dilute sulphuric acid, and not at all by concentrated nitric acid. Frémy obtained chromium in small cubic crystals, by the action of sodium vapour on chromium trichloride at a red-heat. The crystalline chromium resists the action of concentrated acids, even of nitromuriatic acid.

Chromium forms a hexfluoride, CrF_6, and a corresponding oxide, CrO_3, analogous to sulphuric oxide; also, an acid, H_2CrO_4, analogous to sulphuric acid, with corresponding salts, the chromates, which are isomorphous with the sulphates. In its other compounds chromium resembles iron, forming the chromic compounds Cr_2Cl_6, Cr_2O_3, &c., in which it is apparently trivalent but really quadrivalent, and the chromous compounds, $CrCl_2$, CrO, &c., in which it is bivalent.

Chlorides.—The *dichloride*, or *Chromous chloride*, $CrCl_2$, is prepared by heating the violet-coloured trichloride, contained in a porcelain or glass tube, to redness in a current of perfectly dry and pure hydrogen gas: hydrochloric acid is then disengaged, and a white foliated mass is obtained, which dissolves in water with great elevation of temperature, yielding a blue solution, which, on exposure to the air, absorbs oxygen with extraordinary energy, acquiring a deep green colour, and passing into the state of chromic oxychloride, $Cr_2Cl_6.Cr_2O_3$. Chromous chloride is one of the most powerful reducing or deoxidising agents known, precipitating calomel from a solution of mercuric chloride, instantly converting tungstic acid into blue tungsten oxide, and precipitating gold from a solution of auric chloride. It forms, with ammonia, a sky-blue precipitate which turns green on exposure to the air; with ammonia and sal-

circumstances, even at the boiling heat.
assumes the deep-green hydrated stat
exceedingly minute quantity of the di
hydration is marked by the evolution of

The green hydrated chromic chloride is
chromic hydrate in hydrochloric acid, o
or silver chromate, or a solution of chro
acid and a reducing agent, such as alco
even with hydrochloric acid alone :

$$2CrO_3 + 12HCl = Cr_2Cl_6 +$$

The solution thus obtained exhibits
chromic oxygen-salts. When evaporated it
which, when heated to 100° in a stream
mass containing $Cr_2Cl_6.9H_2O$. The sam
vacuum yields green granular crystals co

Fluorides.—The *trifluoride*, or *Chromic*
by treating the dried sesquioxide with hyd
heating the dried mass, as a dark-green s
high temperature, and sublimes when stil
shining regular octohedrons.

The *hexfluoride*, CrF_6, is formed by dist
fluorspar and fuming oil of vitriol in a lea
the vapours in a cooled and dry leaden re
to a blood-red fuming liquid, which volati
rises a few degrees higher. The vapour i
produces violent coughing and severe opp
hexfluoride is decomposed by water, y
chromic acids. A fluoride, intermediate i
two just

hydrogen, being converted into a higher oxide. Chromous oxide is a powerful base, forming pale-blue salts, which absorb oxygen with extreme avidity. Potassio-chromous sulphate has the composition $CrK_2(SO_4)_2.6H_2O$, like the other members of the same group.

Trichromic tetroxide $Cr_3O_4 = CrO.Cr_2O_3$, is the above-mentioned brownish-red precipitate produced by the action of water upon the monoxide. The decomposition is not complete without boiling. This oxide corresponds with the magnetic oxide of iron, and is not salifiable.

Sesquioxide, or *Chromic oxide*, Cr_2O_3.—When mercurous chromate, prepared by mixing solutions of mercurous nitrate and potassium chromate, or dichromate, is exposed to a red heat, it is decomposed, pure chromium sesquioxide, having a fine green colour, remaining. In this state the oxide is, like alumina after ignition, insoluble in acids. The anhydrous sesquioxide may be prepared in a beautifully crystalline form by heating potassium dichromate, $K_2O.2CrO_3$, to full redness in an earthen crucible. One-half of the chromium trioxide contained in that salt then suffers decomposition, oxygen being disengaged and sesquioxide left. The melted mass is then treated with water, which dissolves out neutral potassium chromate, and the oxide is, lastly, washed and dried. Chromium sesquioxide communicates a fine green tint to glass, and is used in enamel painting. The crystalline sesquioxide is employed in the manufacture of razor-strops. From a solution of chromium sesquioxide in potash or soda, green gelatinous hydrated sesquioxide of chromium is separated on standing. When finely powdered and dried over sulphuric acid, it consists of $Cr_2O_3.6H_2O$. A hydrate may also be prepared by boiling a somewhat dilute solution of potassium dichromate strongly acidulated with hydrochloric acid, with small successive portions of sugar or alcohol. In the former case carbon dioxide escapes: in the latter, aldehyde and also acetic acid are formed, and the chromic acid of the salt becomes converted into chromium trichloride, the colour of the liquid changing from red to deep green. The reduction may also be effected, as already observed, by hydrochloric acid alone. A slight excess of ammonia precipitates the hydrate from its solution. It has a pale purplish-green colour, which becomes full green on ignition; a great shrinking of volume and sudden incandescence are observed when the hydrate is decomposed by heat.

Chromium sesquioxide is a weak base, resembling, and isomorphous with, iron sesquioxide and alumina; its salts (chromic salts) have a green or purple colour, and are said to be poisonous.

Chromic sulphate, $(Cr_2)(SO_4)_3$, is prepared by dissolving the hydrated oxide in dilute sulphuric acid. It unites with the sulphates of potassium and ammonium, giving rise to magnificent double salts, which crystallise in regular octohedrons of a deep claret-colour, and possess a constitution resembling that of common alum, the aluminium being replaced by chromium. The ammonium-salt, for example, has the composition $Cr'''(NH_4)(SO_4)_2.12$ aq. The finest crystals are obtained by spontaneous evaporation, the solution being apt to be decomposed by heat.

The *dioxide*, CrO_2, which is, perhaps, a chromic chromate, $CrO_3.Cr_2O_3$, is a brown substance obtained by digesting chromic oxide with excess of chromic acid, or by partial reduction of chromic acid with alcohol, sulphurous acid, &c.

Chromium Trioxide, CrO_3; in combination with water, forming *Chromic acid*, $CrO_3.H_2O = H_2CrO_4 = (CrO_2)''(OH)_2$. Whenever chromium sesquioxide is strongly heated with an alkali, in contact with air, oxygen is absorbed and the trioxide generated. Chromium trioxide may be obtained nearly pure, and in a state of great beauty, by mixing 100 measures of a cold saturated solution of potassium dichromate with 150 measures of oil of vitriol, leaving the whole to cool, pouring off the mother-liquor, and leaving the crystals to drain upon a tile, closely covered by a glass or bell-jar. It is also formed by decomposing the hexfluoride with a small quantity of water. Chromium trioxide crystallises in brilliant crimson-red prisms very deliquescent and soluble in water: the solution is instantly reduced by contact with organic matter.

Chromic acid is bibasic and analogous in composition to sulphuric acid; its salts are isomorphous with the corresponding sulphates.

Potassium chromate, K_2CrO_4 or $(CrO_2)''(OK)_2$.—This salt is made directly from the native *chrome-iron ore*, which is a compound of chromium sesquioxide and ferrous oxide, analogous to magnetic iron ore, by calcination with nitre or with potassium carbonate, or with caustic potash, the ore being reduced to powder and heated for a long time with the alkali in a reverberatory furnace. The product, when treated with water, yields a yellow solution, which, by evaporation, deposits anhydrous crystals of the same colour, isomorphous with potassium sulphate. Potassium chromate has a cool, bitter, and disagreeable taste, and dissolves in 2 parts of water at 15·5°.

Potassium dichromate, or *anhydrochromate*, $K_2O.2CrO_3$ or $K_2CrO_4.CrO_3$.—When sulphuric acid is added to the preceding salt in moderate quantity, one-half of the base is removed, and the neutral chromate converted into dichromate. This salt, of which immense quantities are manufactured for use in the arts, crystallises by slow evaporation in beautiful red tabular crystals, derived from a triclinic prism. It melts when heated, and is soluble in 10 parts of water; the solution has an acid reaction.

Potassium trichromate, $K_2O.3CrO_3$ or $K_2CrO_4.2CrO_3$, may be obtained in crystals by dissolving the dichromate in an aqueous solution of chromic acid, and leaving it to evaporate over sulphuric acid.

Lead chromate, $PbCrO_4$.—This salt, the *chrome-yellow* of the painter, is obtained, as a brilliant yellow precipitate, on mixing solutions of potassium chromate or dichromate with lead nitrate or acetate. On boiling it with lime-water, one-half of the acid is withdrawn, and a basic lead chromate of an orange-red colour left. The basic chromate is also formed by adding lead chromate to fused nitre, and afterwards dissolving out the soluble salts by water: the product is crystalline, and rivals vermilion in beauty of tint. The yellow and orange chrome colours are fixed upon cloth by alternate application of the two solutions, and in the latter case by passing the dyed stuff through a bath of boiling lime-water.

Silver chromate, Ag_2CrO_4.—This salt is precipitated as a reddish brown powder when solutions of potassium chromate and silver nitrate are mixed. It dissolves in hot dilute nitric acid, and separates, on cooling, in small ruby-red platy crystals. The chromates of *barium*, *zinc*, and *mercury* are insoluble; the first two are yellow, the last is brick-red.

Perchromic Acid is obtained, according to Barreswil, by mixing chromic acid with dilute hydrogen dioxide, or potassium dichromate with a dilute but very acid solution of barium dioxide in hydrochloric acid; a liquid is then formed of a blue colour, which is removed from the aqueous solution by ether. This very unstable compound has perhaps the composition $H_2Cr_2O_8$, or $Cr_2O_7.H_2O$, analogous to that of permanganic acid.

Chromium Dioxydichloride, or *Chromyl dichloride*, CrO_2Cl_2, commonly called *Chlorochromic acid*.—When 3 parts of potassium dichromate and 3 parts of common salt are intimately mixed and introduced into a small glass retort, 9 parts of oil of vitriol then added, and heat applied as long as dense red vapours arise, this compound passes over as a heavy deep-red liquid resembling bromine: it is decomposed by water, with production of chromic and hydrochloric acids. It is analogous to the so-called chloromolybdic, chlorotungstic, and chlorosulphuric acids, in composition, and in the products which it yields when decomposed. It may be regarded as formed from the trioxide by substitution of Cl_2 for O, or from chromic acid $(CrO_2)(OH)_2$, by substitution of Cl_2 for $(OH)_2$; also as a compound of chromium hexchloride (not known in the separate state), with chromium trioxide: $CrCl_6.2CrO_3 = 3CrO_2Cl_2$.

Trichromyl dichloride, $(CrO_2)_3Cl_2$ or $CrO_2Cl—CrO_2—CrO_2Cl$ is formed by heating the preceding compound to 180°-190° in a sealed tube: $3CrO_2Cl_2 = (CrO_2)_3Cl_2 + Cl_4$. It is a black noncrystalline powder, which deliquesces rapidly in the air to a dark reddish-brown syrupy liquid smelling of free chlorine. When gently heated in hydrogen gas it takes fire, and is resolved into chromium sesquioxide, hydrochloric acid, and water:

$$2Cr_3O_6Cl_2 + 10H = 3Cr_2O_3 + 4HCl + 3H_2O\,.$$

Reactions of Chromium compounds.—A solution of chromic chloride, or a chromic oxygen salt, is not precipitated or changed in any way by hydrogen sulphide. *Ammonium sulphide* throws down a greyish-green precipitate of chromic hydrate. *Caustic fixed alkalis* also precipitate the hydrated oxide, and dissolve it easily when added in excess. *Ammonia*, the same, but nearly insoluble. The *carbonates*

[illegible]

All chromium compounds, ignited w
alkaline carbonate, yield an alkaline
solved out by water, and on being neut
give the reactions just mentioned.

The oxides of chromium and their sa
blowpipe flame, yield an emerald-gree
is exhibited by those salts of chromi
themselves impart a decided colour to t
the green colour in both flames di
uranium and vanadium, which give gr
only.

URANIU

Atomic weight, 240.

THIS metal is found in a few minerals
oxide, and *uranite*, which is a phosphate
ore. The metal itself is isolated by dec
potassium or sodium, and is obtained a
or in fused white malleable globules, a
which the process is conducted. It i
ordinary temperatures, and does not dec
pulverulent state it takes fire at 207°, b
and forming a dark-green oxide. It uni
chlorine and with sulphur.

Uranium forms two classes of compoun
pounds, in which it is quadrivalent

Uranic oxide or Uranyl oxide, . .	$(UO_2)O$
Uranic oxychloride or Uranyl chloride,	$(UO_2)Cl_2$
Uranic nitrate or Uranyl nitrate, .	$(UO_2)(NO_3)_2$
Uranic sulphate or Uranyl sulphate, .	$(UO_2)(SO_4)$.

This view of the composition of the uranic salts is not, however, essential, since they may also be formulated as basic salts in the manner above illustrated.

Chlorides.—*Uranous chloride*, UCl_4, is formed, with vivid incandescence, by burning metallic uranium in chlorine gas, also by igniting uranous oxide in hydrochloric acid gas. It crystallises in dark-green regular octohedrons, and dissolves easily in water, forming an emerald-green solution, which is decomposed when dropped into boiling water, giving off hydrochloric acid, and yielding a brown precipitate of hydrated uranous oxide. It is a powerful deoxidising agent, reducing gold and silver, converting ferric salts into ferrous salts, &c.

Uranic oxychloride, or *Uranyl chloride*, UO_2Cl_2, is formed when dry chlorine gas is passed over red-hot uranous oxide, as an orange-yellow vapour, which solidifies to a yellow crystalline fusible mass, easily soluble in water. It forms double salts with the chlorides of the alkali-metals,—the potassium salt, for example, having the composition, $UO_2Cl_2.2KCl.2H_2O$.

Oxides.—*Uranous oxide*, UO_2, formerly mistaken for metallic uranium, is obtained by heating the oxide, U_3O_8, or uranic oxalate, in a current of hydrogen. It is a brown powder, sometimes highly crystalline. In the finely divided state it is pyrophoric. It dissolves in acids, forming green salts.

Uranoso-uranic oxide, $U_3O_8 = UO_2.2UO_3$.—This oxide forms the chief constituent of pitchblende. It is obtained artificially by igniting the metal or uranous oxide in contact with the air, or by gentle ignition of uranic oxide or uranic nitrate. It forms a dark-green velvety powder, of specific gravity 7·1 to 7·3. When ignited in hydrogen, or with sodium, charcoal, or sulphur, it is reduced to uranous oxide. When ignited alone, it yields a black oxide, U_2O_5. Uranoso-uranic oxide dissolves in strong sulphuric or hydrochloric acid, yielding a mixture of uranous and uranic salt; by nitric acid it is oxidised to uranic nitrate.

Uranic oxide, or *Uranyl oxide*, UO_3.—Uranium and its lower oxides dissolve in nitric acid, forming uranic nitrate; and when this salt is heated in a glass tube till it begins to decompose, at 250°, pure uranic oxide remains in the form of a chamois-yellow powder. Uranic hydrate, $UO_3.2H_2O$, cannot be prepared by precipitating a uranic salt with alkalis, inasmuch as the precipitate always carries down alkali with it; but it may be obtained by evaporating a solution of uranic nitrate in absolute alcohol at a moderate heat, till, at a certain degree of concentration, nitrous ether, aldehyde, and other vapours are given off, and a spongy yellow mass remains, which is

evaporating to dryness, adding water an
by due evaporation, crystals of uranic n
a repetition of the process, and, lastly
latter solution yields the pure nitrate.

Uranates.—Uranic oxide unites wit
oxides. The uranates of the alkali-metal
ing a uranic salt with a caustic alkali : t
heavy metals, by precipitating a mixtur
of the other metal with ammonia, or by
or acetate of uranium and the other met
example) in contact with the air. The
part, the composition $M_2O.2UO_3$. The
water, soluble in acids. Those which
decomposed at a red heat ; but at a whi
reduced to uranoso-uranic oxide, or by
uranous oxide : the mass obtained by th
fire in contact with the air. *Sodium ur*
used for imparting a yellowish or greeni
yellow pigment on the glazing of porcelai
for these purposes is prepared on the la
blende with lime in a reverberatory furn
calcium uranate with dilute sulphuric ac
uranic sulphate thus obtained with sodiu
uranium is first precipitated together wi
redissolved, tolerably free from impurit
and treating the liquid with dilute sul
down hydrated sodium uranate, $Na_2O.2U$
is but slightly soluble in pure water, an
containing sal-ammoniac ; it may, therefo
tating a solution of sodium-uranate wit
commerce as a fine

Uranic salts are yellow, and yield with *caustic alkalis* a yellow precipitate of alkaline uranate, insoluble in excess of the reagent. *Alkaline carbonates* form a yellow precipitate, consisting of, a carbonate of uranium and the alkali-metal, soluble in excess, especially of acid ammonium or potassium carbonate. *Ammonium sulphide* forms a black precipitate of uranic sulphide. *Hydrogen sulphide* forms no precipitate, but reduces the uranic to a green uranous salt. *Potassium ferrocyanide* forms a red-brown precipitate.

All uranium compounds, fused with *phosphorus salt* or *borax* in the outer blowpipe flame, produce a clear yellow glass, which becomes greenish on cooling. In the inner flame the glass assumes a green colour, becoming still greener on cooling. The oxides of uranium are not reduced to the metallic state by fusion with sodium carbonate on charcoal.

Uranium compounds are used, as already observed, in enamel painting and for the staining of glass, uranous oxide giving a fine black colour, and uranic oxide a delicate greenish-yellow, highly fluorescent glass. Uranium salts are also used in photography.

TUNGSTEN, or WOLFRAM.

Atomic weight, 184. Symbol, W.

TUNGSTEN is found, as ferrous tungstate, in the mineral *wolfram*, tolerably abundant in Cornwall; occasionally also as calcium tungstate (*scheelite* or *tungsten*), and as lead tungstate (*scheeletine*). Metallic tungsten is obtained in the state of a dark-grey powder, by strongly heating tungstic oxide in a stream of hydrogen, but requires for fusion an exceedingly high temperature. It is a white metal, very hard and brittle: it has a density of 17·4. Heated to redness in the air, it takes fire and reproduces tungstic oxide.

Tungsten forms two classes of compounds, in which it is quadrivalent and sexvalent respectively, and a third class, of intermediate composition, in which it is apparently quinquivalent.

Chlorides.—These compounds are formed by heating metallic tungsten in chlorine gas. The *hexchloride*, or *tungstic chloride*, WCl_6, is also produced, together with oxychloride, by the action of chlorine on an ignited mixture of tungstic oxide and charcoal. The oxychlorides, being more volatile than the hexchloride, may be separated from it by sublimation. The hexchloride forms dark violet scales or fused crusts having a bluish-black metallic iridescence. By contact with water or moist air, it is converted into hydrochloric and tungstic acids. The chlorides, WCl_5, WCl_4, and WCl_2, are formed when the hexchloride is heated in hydrogen gas. The two former are crystalline: the dichloride is a loose grey powder, destitute of crystalline structure.*

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* Roscoe, Journal of the Chemical Society, 1872, p. 287.

takes the electro-positive part.
acid tendencies, uniting with bas
crystallisable salts called *tungsta*
regarded as a compound of the othe

The *dioxide*, or *Tungstous oxide*, W
exposing tungstic oxide to hydrogen,
dull redness. It is a brown p
crystalline appearance and an impe
fire when heated in the air, and b
tungstic oxide. It forms a definite

The *trioxide*, or *Tungstic oxide*, W
native calcium tungstate by digestio
the soluble calcium salt thereby pr
water, and the remaining tungstic a
may be prepared by repeatedly di
hydrochloric acid, ultimately with a
to dissolve out the iron and mangan
tungstic acid in aqueous ammonia;
heating the residual ammonium tun
Tungstic oxide is a yellow powder in
acids, but soluble in alkalis. The h
alkaline tungstates, when neutralised
precipitate of *tungstic monohydrate*
$H_2O.WO_3$. Cold dilute solutions, o
acids a white precipitate, consisting of
tungstic acid, $2H_2O.WO_3$ or H_2WO_4,
litmus and dissolves easily in alkalis.

Tungstates.—Tungstic acid unit
often in very unusual proportions.
in two isomeric modifications

tungstic acid with zinc and hydrochloric acid; also by heating ammonium tungstate to redness in a retort.

Metatungstates.—These salts, which have the composition of quadracid tungstates, $M_2O.4WO_3$, are formed from ordinary tungstates by addition of tungstic acid, or by removing part of the base by means of an acid. They are for the most part soluble and crystallisable. By decomposing barium metatungstate with dilute sulphuric acid, and evaporating the filtrate in a vacuum, hydrated metatungstic acid is obtained in quadratic octohedrons apparently containing $H_2O.4WO_3+31$ aq.; it is very soluble in water.

*Silicotungstates.**—By boiling gelatinous silica with acid potassium tungstate, a crystalline salt is obtained, having the composition of a diacid potassium tungstate, $6(K_2O.2WO_3)$, or $K_{12}O_6.12WO_3$, in which one-third of the potassium is replaced by silicon, viz., $K_8Si^{iv}O_6.12WO_3$, so that the silicon here enters as a *basylous* element. The resulting solution yields with mercurous nitrate a precipitate of *mercurous silicotungstate*; this, when decomposed by an equivalent quantity of hydrochloric acid, yields a solution of *hydrogen silicotungstate*, or *silicotungstic acid*; and the other silicotungstates, which are all soluble, are obtained by treating the acid with carbonates.

Silicodecitungstic acid, $H_8Si^{iv}O_6.10WO_3$, is obtained as an ammonium salt by boiling gelatinous silica with solution of acid ammonium tungstate; and from this, the acid and its other salts may be obtained in the same manner as the preceding. The silicodecitungstates are very unstable, and the acid is decomposed by mere evaporation, depositing silica, and being converted into *tungstosilicic acid*, which is isomeric with silicotungstic acid, and likewise decomposes carbonates. All three of these acids are capable of exchanging either one-half or the whole of their basic hydrogen for metals, thereby forming acid and neutral salts; silicotungstic acid also forms an acid sodium salt in which only one-fourth of the hydrogen is replaced by sodium.

Tungsten Sulphides.—The *disulphide*, or *Tungstous sulphide*, WS_2, is obtained in soft, black, needle-shaped crystals by igniting tungsten, or one of its oxides, with sulphur.

The *trisulphide*, or *Tungstic sulphide*, WS_3, is formed by dissolving tungstic acid in ammonium sulphide, and precipitating with an acid, or by adding hydrochloric acid to the solution of an alkaline tungstate saturated with hydrogen sulphide. It is a light-brown precipitate, turning black when dry. It unites easily with basic metallic sulphides, forming the *sulphotungstates*, M_2WS_4, analogous to the normal tungstates.

Reactions of Tungsten compounds.—Soluble tungstates, or metatungstates, supersaturated with sulphuric, hydrochloric, phosphoric,

* Marignac, Ann. Chim. Phys. [4] iii. 5; Watts's Dictionary of Chemistry, v. 915.

oxalic, or acetic acid, yield, on the introduction of a piece of *zinc*, a beautiful blue colour, arising from the formation of blue tungsten oxide. A soluble tungstate, mixed with *ammonium sulphide*, and then with excess of acid, yields a light-brown precipitate of tungstic sulphide, soluble in ammonium sulphide. *Hydrogen sulphide* does not precipitate the acidulated solution of a tungstate, but turns it blue, owing to the formation of the blue oxide. Ordinary tungstates give, with *potassium ferrocyanide*, after addition of hydrochloric acid, a brown flocculent precipitate, soluble in pure water free from acid; metatungstates give no precipitate. *Acids*, added to solutions of ordinary tungstates, throw down a white or yellow precipitate of tungstic acid; with metatungstates no precipitate is obtained.

All tungsten compounds form colourless beads with borax and phosphorus salt, in the outer blowpipe flame. With *borax*, in the inner flame, they form a yellow glass, if the quantity of tungsten is somewhat considerable, but colourless with a smaller quantity. With *phosphorus salt* in the inner flame they form a glass of a pure blue colour, unless metallic oxides are present, which modify it; in presence of iron the glass is blood-red, but the addition of metallic tin renders it blue.

Steel, alloyed with a small quantity of tungsten, acquires extraordinary hardness. Wootz, or Indian steel, contains tungsten. Tungsten has also a remarkable effect on steel in increasing its power of retaining magnetism when hardened. A horse-shoe magnet of ordinary steel, weighing two pounds, is considered of good quality when it bears seven times its own weight; but, according to Siemens, a similar magnet made with steel containing tungsten may be made to carry twenty times its weight suspended from the armature.*

MOLYBDENUM.

Atomic weight, 96. Symbol, Mo.

THIS metal occurs in small quantity as sulphide, or *molybdenite*, and as lead molybdate, or *wulfenite*. Metallic molybdenum is obtained by exposing molybdic oxide in a charcoal-lined crucible to the most intense heat that can be obtained. It is a white, brittle, and exceedingly infusible metal, having a density of 8·6, and oxidising, when heated in the air, to molybdic oxide.

Chlorides.—Molybdenum forms four chlorides, containing $MoCl_2$ $MoCl_3$, or Mo_2Cl_6, $MoCl_4$ and $MoCl_5$ or Mo_2Cl_{10}.

The *pentachloride* is produced when metallic molybdenum (previously freed from oxide by ignition in hydrogen chloride) is heated for some time in a stream of dry chlorine gas.

* Journal of the Chemical Society, July, 1868. 2nd Series, vol. vi. p. 284.

The pentachloride, heated to about 250° in a stream of hydrogen, is reduced to the red, difficulty volatile **trichloride**, $MoCl_3$ or Mo_2Cl_6; and this compound, heated to redness in an atmosphere of carbon dioxide free from oxygen, is resolved, according to the equation $Mo_2Cl_6 = MoCl_2 + MoCl_4$ into the yellow **dichloride** which remains in the tube, and the brown **tetrachloride** which sublimes or is carried forward by the stream of gas.

Of these four chlorides the pentachloride is the only one which crystallises distinctly, and melts and volatilises without decomposition. The pure pentachloride is black. Its vapour has a dark brown-red colour. The sulphur-yellow dichloride and the red trichloride, which is deceptively like amorphous phosphorus, have been obtained only in the amorphous state; the tetrachloride is an indistinctly crystalline brown sublimate. In an atmosphere of carbon dioxide the dichloride bears a bright red heat without melting or volatilising; the trichloride under the same circumstances is resolved into di- and tetrachloride, which when again heated splits up into pentachloride which sublimes, and trichloride which remains behind.

The di- and trichloride are quite permanent in the air at ordinary temperatures, and insoluble in water; the tetra- and pentachloride, on the other hand, are extremely susceptible of the action of oxygen, and more particularly of moisture.

The dichloride is insoluble in *nitric acid*, which, however, dissolves all the other chlorides. The dichloride dissolves easily in hot *hydrochloric acid*, with aid of heat, and crystallises therefrom on cooling, in long, shining, yellow needles, $Mo_2Cl_4.3H_2O$, which give off $2H_2O$ at 100°.*

The *bromides* of molybdenum correspond in composition with the chlorides; there is also an oxybromide containing $Mo^{vi}Br_2O_2$.

Fluorides.—Molybdenum forms three fluorides, MoF_2, MoF_4, and MoF_6, which are obtained by dissolving the corresponding oxides in hydrofluoric acid. The *hexfluoride* is not known in the free state, but only in combination with basic metallic fluorides and molybdates; thus there is a potassium salt containing $K_2MoO_4.K_2MoF_8$.

Oxides.—Molybdenum forms the three oxides, MoO, MoO_2, and MoO_3, besides several oxides intermediate between the last two, which may be regarded as molybdic molybdates.

The *monoxide*, or *Molybdous oxide*, MoO, is produced by bringing the dioxide or trioxide, in presence of one of the stronger acids, in contact with any of the metals which decompose water. Thus when zinc is immersed in a concentrated solution of an alkaline molybdate mixed with a quantity of hydrochloric acid sufficient to redissolve the precipitate first thrown down, zinc chloride and molybdous chloride are formed. The dark-coloured solution thus obtained is mixed with a large quantity of caustic potash, which precipitates a black hydrated molybdous oxide, and retains the zinc oxide in solution. The freshly precipitated hydrate is soluble in acids and ammonium carbonate; when heated in the air it burns to dioxide, but when dried in a vacuum it leaves the black anhydrous monoxide.

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* Liechti and Kempi, Liebig's Annalen, c. lxix. 344.

The *dioxide*, or *Molybdic oxide*. MoO_2, is obtained in the anhydrous state by heating sodium molybdate with sal-ammoniac, the molybdic trioxide being reduced to dioxide by the hydrogen of the ammoniacal salt; or, in the hydrated state, by digesting metallic copper in a solution of molybdic acid in hydrochloric acid, until the liquid assumes a red colour, and then adding a large excess of ammonia. The anhydrous dioxide is deep brown, and insoluble in acids; the hydrate resembles ferric hydrate, and dissolves in acids, yielding red solutions. It is converted into molybdic acid by strong nitric acid.

Trioxide MoO_3.—To obtain this oxide (commonly called *Molybdic acid*) native molybdenum sulphide is roasted, at a red heat, in an open vessel, and the impure molybdic trioxide thence resulting is dissolved in ammonia. The filtered solution is evaporated to dryness, and the salt is taken up by water and purified by crystallisation. It is, lastly, decomposed by heat, and the ammonia expelled. The trioxide may also be prepared by decomposing native lead molybdate with sulphuric acid. It is a white crystalline powder, fusible at a red heat, and slightly soluble in water. The solution contains *molybdic acid*, but this acid, or hydrate, is not known in the solid state. The trioxide is easily dissolved by alkalis, and forms two series of salts, viz., *normal* or *neutral molybdates*, R_2MoO_4, or $R_2O.MoO_3$, and *anhydromolybdates*, or *bimolybdates* $R_2MoO_4.MoO_3$, or $R_2O.2MoO_3$, the symbol R denoting a univalent metal. The neutral molybdates of the alkali-metals are easily soluble in water, and their solutions yield, with the stronger acids, a precipitate, either of a less soluble bimolybdate, or of the anhydrous trioxide. The other molybdates are insoluble, and are obtained by precipitation. *Lead Molybdate*, $PbMoO_4$, occurs native in yellow quadratic plates and octohedrons.

Sulphides.—Molybdenum forms three sulphides, MoS_2, MoS_3, and MoS_4, the last two of which are acid sulphides, forming sulphur-salts. The *disulphide*, or *Molybdic sulphide*, MoS_2, occurs native, as *molybdenite* in crystallo-laminar masses, or tabular crystals, having a strong metallic lustre and lead-grey colour, and forming a grey streak on paper, like plumbago. The same compound is produced artificially by heating either of the higher sulphides, or by igniting the trioxide with sulphur. When roasted in contact with the air, it is converted into trioxide.

The *trisulphide*, MoS_3, commonly called *Sulphomolybdic acid*, is obtained by passing hydrogen sulphide into a concentrated solution of an alkaline molybdate, and precipitating with an acid. It is a black-brown powder, which is dissolved slowly by alkalis, more easily by alkaline sulphides and sulphydrates, forming sulphur salts called *Sulphomolybdates*. Most of these salts have the composition R_2MoS_4, or $R_2S.MoS_3$, analogous to that of the molybdates.

The sulpho-molybdates of the alkali-metals, alkaline earth-metals, and magnesium, are soluble in water, forming solutions of a fine red colour; the rest are insoluble.

Tetrasulphide, MoS_4.—This is also an acid sulphide, forming salts called *persulphomolybdates*, the general formula of which is R_2MoS_5, or $R_2S.MoS_4$. The *potassium salt* is obtained by boiling the sulphomolybdate with molybdenum trisulphide.

Molybdous salts, obtained by dissolving molybdous oxide in acids, are opaque and almost black. They yield, with *hydrogen sulphide*, a brown-black precipitate soluble in ammonium sulphide; with *alkalis* and *alkaline carbonates*, a brownish-black precipitate of molybdous hydrate, easily soluble in acid potassium carbonate, or in ammonium carbonate; with *potassium ferrocyanide*, a dark brown precipitate; with *sodium phosphate*, a white precipitate.

Solutions of molybdic salts have a reddish-brown colour. When heated in the air, they have a tendency to become blue by oxidation. In contact with metallic *zinc*, they first blacken and then yield a black precipitate of molybdous hydrate. Their reactions with *alkalis*, *hydrogen sulphide*, &c., are similar to those of molybdous salts; but the precipitates are lighter in colour.

Molybdates are colourless unless they contain a coloured base. Solutions of the alkaline molybdates yield with *acids* a precipitate of molybdic trioxide, soluble in excess of the precipitant. They are coloured yellow by *hydrogen sulphide*, from formation of a sulphomolybdate of the alkali-metal, and then yield with acids a brown precipitate of molybdenum trisulphide. This is an extremely delicate test for molybdic acid. They form white precipitates with the salts of the *earth-metals*, and precipitates of various colours with salts of the *heavy metals*. When *ortho-phosphoric acid*, or a liquid containing it, is added to the solution of ammonium molybdate, together with an excess of hydrochloric acid, the liquid turns yellow, and after a while deposits a yellow precipitate of molybdic trioxide, combined with small quantities of phosphoric acid and ammonia. This precipitate is soluble in ammonia and likewise in excess of the phosphate. The reaction is therefore especially adapted for the detection of small quantities of phosphoric acid. The pyrophosphates and metaphosphates do not produce the yellow precipitate. *Arsenic acid* gives a similar reaction.

All the oxides of molybdenum form, with *borax*, in the outer blowpipe flame, a bead which is yellow while hot, and colourless on cooling; in the inner flame, a dark brown bead, which is opaque if excess of molybdenum is present. By long continued heating, the molybdic oxide may be separated in dark brown flakes, floating in the clear yellow glass. With *phosphorus salt* in the outer flame, all oxides of molybdenum give a bead which is greenish while hot, and colourless on cooling; in the inner flame a clear green bead, from which molybdic oxide cannot be separated by continued heating.

CLASS VII.—HEPTAD METALS.

MANGANESE, as already observed, is the only known metal referable to this class, and it is more conveniently described in connection with the iron metals.

CLASS VIII.—GROUP I.—IRON METALS.

IRON.

Atomic weight, 56. Symbol, Fe (Ferrum).

THIS is the most important of all the metals: there are few substances to which it yields in interest, when it is considered how very intimately the knowledge of its properties and uses is connected with human civilisation.

Metallic iron is of exceedingly rare occurrence: it has been found at Canaan, in Connecticut, forming a vein about two inches thick in mica-slate; but it enters into the composition of many of those extraordinary stones known to fall from the air, called *meteorites*. Isolated masses of soft maleable iron also, of large dimensions, lie loose upon the surface of the earth in South America and elsewhere, and are presumed to have had a similar origin: these latter, in common with the iron of the undoubted meteorites, contain nickel. In an oxidised condition, the presence of iron may be said to be universal: it constitutes a great part of the common colouring matter of rocks and soils; it is contained in plants, and forms an essential component of the blood of the animal body. It is also very common in the state of bisulphide. Pure iron may be prepared, according to Mitscherlich, by introducing into a Hessian crucible 4 parts of fine iron wire cut small, and 1 part of black iron oxide. This is covered with a mixture of white sand, lime, and potassium carbonate, in the proportions used for glass-making, and a cover being closely applied, the crucible is exposed to a very high degree of heat. A button of pure metal is thus obtained, the traces of carbon and silicon present in the wire having been removed by the oxygen of the oxide.

Pure iron has a white colour and perfect lustre: it is extremely soft and tough, and has a specific gravity of 7·8. Its crystalline form is probably the cube, to judge from appearances occasionally exhibited. In good bar-iron or wire, a distinct fibrous texture may always be observed when the metal has been attacked by rusting or by the application of an acid, and upon the perfection of this fibre much of its strength and value depends. Iron is the most tenacious of all the metals, a wire $\frac{1}{36}$ of an inch in diameter bearing a weight of 60 lbs. It is very difficult of fusion, and before becoming liquid passes through a soft or pasty condition. Pieces of iron, pressed or hammered together in this state, cohere into a single mass: the operation is termed *welding*, and is usually performed by sprinkling a little sand over the heated metal, which combines with the superficial film of oxide, forming a fusible silicate, which is subsequently forced out from between the pieces of iron by the pressure applied: clean surfaces of metal are thus presented to each other, and union takes place without difficulty.

Iron does not oxidise in dry air at common temperatures: heated to redness, it becomes covered with a scaly coating of black oxide, and at a high white heat burns brilliantly, producing the same substance. In oxygen gas the combustion occurs with still greater ease. The finely divided spongy metal, prepared by reducing the red oxide with hydrogen gas, takes fire spontaneously in the air. Pure water, free from air and carbonic acid, does not tarnish a surface of polished iron, but the combined agency of free oxygen and moisture speedily leads to the production of rust, which is a hydrate of the sesquioxide. The rusting of iron is wonderfully promoted by the presence of a little acid vapour. At a red heat, iron decomposes water, evolving hydrogen, and passing into the black oxide. Dilute sulphuric and hydrochloric acids dissolve it freely, with separation of hydrogen. Iron is strongly magnetic up to a red heat, when it loses all traces of that remarkable property.

Iron forms two classes of compounds; namely the ferrous compounds, in which it is bivalent, *e.g.*, $FeCl_2$, FeO, $FeSO_4$, &c., and the ferric compounds, in which it may be regarded either as trivalent like aluminium, or as quadrivalent: ferric chloride, for example, may be either $FeCl_3$ or $Fe_2Cl_6 = Cl_3Fe—FeCl_3$; the vapour-density of this compound, as determined by Deville, is in favour of the latter formula.

Chlorides.—The *dichloride*, or *Ferrous chloride*, $FeCl_2$, is formed by transmitting dry hydrochloric acid gas over red-hot metallic iron, or by dissolving iron in hydrochloric acid. The latter solution yields, when duly concentrated, green crystals of the hydrated dichloride, $FeCl_2.4H_2O$; they are very soluble and deliquescent, and rapidly oxidise in the air.

The *trichloride*, or *Ferric chloride*, Fe_2Cl_6, is usually prepared by dissolving ferric oxide in hydrochloric acid. The solution, evaporated to a syrupy consistence, deposits red hydrated crystals, which are very soluble in water and alcohol. It forms double salts with potassium chloride and sal-ammoniac. When evaporated to dryness and strongly heated, much of the chloride is decomposed, yielding sesquioxide and hydrochloric acid: the remainder sublimes, and afterwards condenses in the form of small brilliant red crystals, which deliquesce rapidly. Anhydrous ferric chloride is also produced by the action of chlorine upon the heated metal. The solution of ferric chloride is capable of dissolving a large excess of recently precipitated ferric hydrate, by which it acquires a much darker colour.

Iodides.—*Ferrous iodide*, FeI_2, is an important medicinal preparation: it is easily made by digesting iodine with water and metallic iron. The solution is pale-green, and yields, on evaporation, crystals resembling those of the chloride, which rapidly oxidise on exposure to air. It is best preserved in solution in contact with excess of iron.—*Ferric iodide*, Fe_2I_6, is yellowish-red and soluble.

Iron Oxides and Oxysalts.—Three oxides of iron are known, namely, ferrous oxide, FeO, and ferric oxide Fe_2O_3, analogous to the chlorides, and an intermediate oxide, usually called magnetic iron oxide, containing Fe_3O_4 or $FeO.Fe_2O_3$. A trioxide, FeO_3, is supposed to exist in a class of salts called ferrates, but it has not been isolated.

Monoxide, or *Ferrous oxide*, FeO.—This is a very powerful base, neutralising acids, and isomorphous with magnesia, zinc oxide, &c. It is almost unknown in the separate state, from its extreme proneness to absorb oxygen and pass into the sesquioxide. When a ferrous salt is mixed with caustic alkali or ammonia, a bulky whitish precipitate of ferrous hydrate falls, which becomes nearly black when boiled, the water being separated. This hydrate changes very rapidly when exposed to the air, becoming green and ultimately red-brown. The soluble ferrous salts have commonly a delicate pale-green colour and a nauseous metallic taste.

Sesquioxide, or *Ferric oxide*, Fe_2O_3.—A feeble base, isomorphous with alumina. It occurs native, most beautifully crystallised, as specular iron ore, in the island of Elba, and elsewhere; also as red and brown *hæmatite*, the latter being a hydrate. It is artificially prepared by precipitating a solution of ferric sulphate or chloride with excess of ammonia, and washing, drying, and igniting the yellowish-brown hydrate thus produced: fixed alkali must not be used in this operation, as a portion is retained by the oxide. In fine powder, this oxide has a full red colour, and is used as a pigment, being prepared for the purpose by calcination of ferrous sulphate; the tint varies somewhat with the temperature to which it has been exposed. The oxide is unaltered in the fire, although easily reduced at a high temperature by carbon or hydrogen. It dissolves in acids, with difficulty after strong ignition, forming a series of reddish salts, which have an acid reaction and an astringent taste. Ferric oxide is not acted upon by the magnet.

Triferro-tetroxide, *Ferroso-ferric oxide*, $Fe_3O_4 = FeO.Fe_2O_3$, also called black *iron oxide*, *magnetic oxide*, and *loadstone*, a natural product, one of the most valuable of the iron-ores, often found in regular octohedral crystals, which are magnetic. It may be prepared by mixing due proportions of ferrous and ferric salts, precipitating them with excess of alkali, and then boiling the mixed hydrates; the latter then unite to a black sandy substance, consisting of minute crystals of the magnetic oxide. This oxide is the chief product of the oxidation of iron at a high temperature in the air and in aqueous vapour. It is incapable of forming definite salts.

FERRATES.—When a mixture of one part of pure ferric oxide and four parts of dry nitre is heated to full redness for an hour in a covered crucible, and the resulting brown, porous, deliquescent mass is treated when cold with ice-cold water, a deep amethystine-red solution of potassium ferrate is obtained. The same salt may be more easily prepared by passing chlorine gas through a strong solution of potash in which recently precipitated ferric hydrate is suspended; it is then deposited as a black powder, which may be drained upon a tile. It consists of K_2FeO_4 or $K_2O.FeO_3$, and is therefore analogous in composition to the sulphate and chromate of potassium. The solution of this salt gradually decomposes, even in the cold, and rapidly when heated, giving off oxygen and depositing sesquioxide. The solution of potassium ferrate gives no precipitate with salts of calcium, magnesium, or strontium, but when mixed with a barium salt, it yields a deep crimson, insoluble *barium ferrate*, $BaFeO_4$ or $BaO.FeO_3$, which is very permanent. Neither the hydrogen-salt or ferric acid, H_2FeO_4, nor the corresponding anhydrous oxide, FeO_3, is known in the separate state.

FERROUS SULPHATE, $FeSO_4.7H_2O$ or $FeO.SO_3.7H_2O$.—This beautiful and important salt, commonly called *green vitriol*, *iron vitriol*, or *copperas*, may be obtained by dissolving iron in dilute sulphuric acid: it is generally prepared, however, and on a very large scale, by contact of air and moisture with common iron pyrites, which, by absorption of oxygen, readily furnishes the substance in question. Heaps of this material are exposed to the air until the decomposition is sufficiently advanced: the salt produced is then dissolved out by water, and the solution made to crystallise. It forms large green crystals, of the composition above stated, which slowly effloresce and oxidise in the air: it is soluble in about twice its weight of cold water. Crystals containing 4 and also 2 molecules of water have been obtained. Ferrous sulphate forms double salts with the sulphates of potassium and ammonium, containing $FeK_2(SO_4)_2.6H_2O$ and $Fe(NH_4)_2(SO_4)_2.6H_2O$, isomorphous with the corresponding magnesium salts.

FERRIC SULPHATE, $(Fe_2)^{vi}(SO_4)_3$ or $Fe_2O_3.3SO_3$, is prepared by adding to a solution of the ferrous salt exactly one-half as much sulphuric acid as it already contains, raising the liquid to the boiling-point, and then dropping in nitric acid until the solution ceases to blacken by such addition. The red liquid thus obtained furnishes, on evaporation to dryness, a buff-coloured amorphous mass, which dissolves very slowly when put into water. With the sulphates of potassium and ammonium, this salt yields compounds having the form and constitution of alums; the potassium salt, for example, has the composition $Fe'''K(SO_4)_2 12H_2O$. The crystals are nearly des-

Ferric nitrate is readily formed by
diluted, upon iron: it is a deep-red l
soluble basic salt, and is used in dyeing

Ferrous Carbonate, $FeCO_3$ or FeO
tate obtained by mixing solutions o
carbonate: it cannot be washed and d
acid and absorbing oxygen. This sul
spathose iron ore, or *iron spar*, associate
calcium and magnesium carbonates; al
stone, from which nearly all the Britis
found in mineral waters, being soluble
such waters are known by the rusty mat
to the air. No ferric carbonate is know
The *phosphates* of iron are all insolubl

Iron Sulphides.—Several compo
known: of these the two most import
monosulphide, or *ferrous sulphide*, FeS, is
attracted by the magnet, formed by
sulphur. It is dissolved by dilute acids
etted hydrogen gas, and is constantly e
the laboratory, being made by projectin
mixture of 2½ parts of sulphur and 4 pa
of cast iron, and excluding the air as m
substance is formed when a bar of wh
contact with sulphur. The *bisulphide*,
natural product, occurring in rocks of all
in many cases by the gradual deoxidat
organic matter. It has a brass-yellow
attracted by the magnet, and not acted

little is known respecting them in a definite state. The carbonide is contained in cast iron and in steel, to which it communicates ready fusibility; the silicon-compound is also found in cast iron. Phosphorus is a very hurtful substance in bar iron, as it renders it brittle or *cold-short.*

REACTIONS OF IRON SALTS.—Ferrous salts are thus distinguished:

Caustic alkalis and *ammonia* give nearly white precipitates, insoluble in excess of the reagent, rapidly becoming green, and ultimately brown, by exposure to air. The *carbonates* of *potassium, sodium*, and *ammonium* throw down whitish ferrous carbonate, also very subject to change. *Hydrogen sulphide* gives no precipitate, but *ammonium sulphide* throws down black ferrous sulphide, soluble in dilute acids. *Potassium ferrocyanide* gives a nearly white precipitate, becoming deep-blue on exposure to air; the *ferricyanide* gives at once a deep-blue precipitate.

Ferric salts are thus characterised:

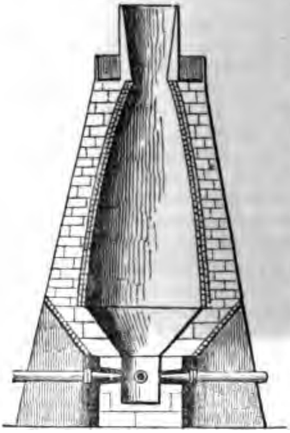
Caustic fixed alkalis and *ammonia* give foxy-red precipitates of ferric hydrate, insoluble in excess.

The *carbonates* behave in a similar manner, the carbonic acid escaping. *Hydrogen sulphide* gives a nearly white precipitate of sulphur, and reduces the sesquioxide to monoxide. *Ammonium sulphide* gives a black precipitate, slightly soluble in excess. *Potassium ferrocyanide* yields Prussian blue. Tincture or infusion of *gall-nuts* strikes intense bluish-black with the most dilute solutions of ferric salts.

Iron Manufacture.—This most important branch of industry consists, as now conducted, of two distinct parts—viz., the production from the ore of a fusible carbonide of iron, and the subsequent decomposition of the carbonide, and its conversion into pure or malleable iron.

The clay-iron ore is found in association with coal, forming thin beds or nodules: it consists, as already mentioned, of ferrous carbonate mixed with clay; sometimes lime and magnesia are also present. It is broken in pieces, and exposed to heat in a furnace resembling a lime-kiln, by which the water and carbonic acid are expelled, and the ore rendered dark-coloured, denser, and also magnetic: it is then ready for reduction. The furnace in which this operation is performed is usually of very large dimensions, 50 feet or more in height, and constructed of brickwork with great solidity, the interior being lined with excellent fire-bricks: the shape will be understood from the section shown in fig. 154. The furnace is close at the bottom, the fire being maintained by a powerful artificial blast introduced by two or three *twyere-pipes*, as shown in the section. The materials, consisting of due proportion of coke or carbonised coal, roasted ore, and limestone, are constantly

Fig. 154.



supplied from the top, the operation proceeding continuously night and day, often for years, or until the furnace is judged to require repair. In the upper part of the furnace, where the temperature is still very high, and where combustible gases abound, the iron of the ore is probably reduced to the metallic state, being disseminated through the earthy matter of the ore. As the whole sinks down and attains a still higher degree of heat, the iron becomes converted into carbonide by *cementation*, while the silica and alumina unite with the lime, purposely added, to a kind of glass or *slag*, nearly free from iron oxide. The carbonide and slag, both in a melted state, reach at last the bottom of the furnace, where they arrange themselves in the order of their densities: the slag flows out at certain apertures contrived for the purpose, and the iron is discharged from time to time, and suffered to run into rude moulds of sand by opening an orifice at the bottom of the recipient, previously stopped with clay. Such is the origin of *crude*, *cast*, or *pig iron*, of which there are several varieties, distinguished by differences of colour, hardness, and composition, and known by the names of *grey*, *black*, and *white* iron. The first is for most purposes the best, as it admits of being filed and cut with perfect ease. The black and grey kinds probably contain a mechanical admixture of graphite, which separates during solidification.

A great improvement in the original mode of conducting the process was the substitution of raw coal for coke, and the blowing of hot air instead of cold into the furnace. This is effected by causing the air, on leaving the blowing-machine, to circulate through a system of red-hot iron pipes, until its temperature becomes high enough to melt lead. This alteration effects a prodigious saving in fuel, without injury to the quality of the product.

The conversion of cast into bar iron is effected chiefly by an operation called *puddling*, previous to which, however, it sometimes undergoes a process called *refining*, which consists in remelting it, in contact with the fuel, in small low furnaces called *refineries*, while air is blown over its surface by means of twyeres. The effect of this operation is to deprive the iron of a great part of the carbon and silicon associated with it. The metal thus purified is run out into a trench, and suddenly cooled, by which it becomes white, crystalline, and exceedingly hard: in this state it is called *fine metal*. The puddling process is conducted in an ordinary reverberatory furnace, into which the charge of crude or of fine metal is introduced by a side aperture. This is speedily melted by the flame, and its surface covered with a crust or oxide. The workman then, by the aid of an iron tool, diligently stirs the melted mass, so as intimately to mix the oxide with the metal; he now and then also throws in a little water, with the view of promoting more rapid oxidation. Small jets of blue flame soon appear upon the surface of the iron, and the latter, after a time, begins to lose its fluidity, and acquires, in succession, a pasty and a granular condition. At this point the fire is strongly urged, the sandy particles once more cohere, and the contents of the furnace now admit of being formed into several large balls or masses, which are then withdrawn, and placed under an immense hammer, moved by machinery, by which each becomes quickly fashioned into a rude bar. This is reheated, and passed between grooved cast-iron rollers, and drawn out into a long bar or rod. To make the best iron, the bar is cut into a number of pieces, which are afterwards piled or bound together, again raised to a welding heat, and hammered or rolled into a single bar; and this process of *piling* or *fagoting* is sometimes twice or thrice repeated, the iron becoming greatly improved thereby.

The general nature of the change in the puddling furnace is not difficult to explain. Cast iron consists essentially of iron in combination with carbon and silicon. When strongly heated with iron oxide, those compounds undergo decomposition, the carbon and silicon becoming oxidised at the expense of the oxygen of the oxide. As this change takes place, the metal gradually loses its fusibility, but retains a certain degree of adhesiveness, so that when at last it comes under the tilt-hammer, or between the rollers, the particles of iron become agglutinated into a solid mass, while the readily fusible silicate of the oxide is squeezed out and separated.

All these processes are, in Great Britain, performed with coal or coke; but the iron obtained is, in many respects, inferior to that made in Sweden and Russia from the magnetic oxide, by the use of wood charcoal—a fuel too dear to be extensively employed in England. Plate iron is, however, sometimes made with charcoal.

A method of producing malleable iron directly from the ore has been invented by C. W. Siemens.* The furnace consists of a rotatory iron cylinder, which, by means of wheel-gearing, may be made to revolve either four or five times or from 60 to 80 times in an hour. The ore to be smelted is broken into fragments not exceeding the size of peas or beans; and to it is added lime or other fluxing material, in such proportion that the gangue contained in the ore and flux combines with only a little ferrous oxide into basic and fluid slag. If the ore is hæmatite, or contains silica, it is best to add alumina in the shape of aluminous iron ore; manganiferous iron ore may also be added with advantage. A charge of about 20

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* Chem. Soc. Jour., 1874, p. 671; Watts's Dictionary of Chemistry, 2d Suppl., p. 701.

cipitated by each piece of carbon, wh
a fluid slag with the siliceous gangue
action is then again resorted to, whe
and over, presenting continually new
and to the flame within the rotator.

When the reduction of the iron
rotator is stopped in the proper posi
cinder ; after this the quick speed
whereby the loose masses of iron con
lected into two or three metallic ball
shingled in the usual way of consolid
nace is tapped again, and is ready to r

Steel.—A very remarkable and m
by heating iron in contact with charco
imbedded in charcoal powder, conta
crucible or chest of some substance ca
exposed for many hours to a full red he
these circumstances, from 1·3 to 1·7 p
harder, and at the same time fusible
however, of malleability. The activ
process is probably carbon monoxide
the crucible combines with the carbon
is afterwards decomposed by the heate
being abstracted by the latter. The
takes up an additional dose of carbon
becomes monoxide, the oxygen, or rath
as a carrier between the charcoal and
this operation is called *blistered* steel, f
appearance of the bars: the texture
equalised by welding a number of th

The quantity of tungsten thus absorbed by the iron is very small, and some chemists attribute the properties of the so-called tungsten steel to the general treatment rather than to the presence of tungsten.

The most perfect kind of steel is that which has undergone fusion, having been cast into ingot moulds, and afterwards hammered: of this all fine cutting instruments are made. It is difficult to forge, requiring great skill and care on the part of the operator.

Steel may also be made directly from some particular varieties of cast iron, as that from spathose iron ore containing a little manganese. The metal is retained, in a melted state, on the hearth of a furnace, while a stream of air plays upon it, and causes partial oxidation: the oxide produced reacts, as before stated, on the carbon of the iron, and withdraws a portion of that element. When a proper degree of stiffness or pastiness is observed in the residual metal, it is withdrawn, and hammered or rolled into bars. The *wootz*, or native steel of India, is probably made in this manner. Annealed cast iron, sometimes called *run steel*, is now much employed as a substitute for the more costly products of the forge: the articles when cast, are imbedded in powdered iron ore, or some earthy material, and, after being exposed to a moderate red heat for some time, are allowed to cool slowly, by which a very great degree of softness and malleability is attained. It is very possible that some little decarbonisation may take place during this process.

Cast steel may also be made in Siemens's rotatory furnace above described, the balls being transferred from the rotator to the bath of a steel-melting furnace in their heated condition, and without subjecting them to previous consolidation under a hammer or shingling machine. It is possible, however, to push the operation within the rotator to the point of obtaining cast steel. For this purpose the relative amount of carbonaceous matter is somewhat increased in the first instance, so that the ball, if shingled, would be of the nature of puddled steel, or even contain some carbon mechanically mixed.

Bessemer steel is produced by forcing atmospheric air into melted cast iron. The carbon being oxidised more readily than the iron, it is converted into carbon monoxide, which escapes in a sufficiently heated state to take fire on coming in contact with atmospheric air. Considerable heat is generated by the oxidation of the carbon and iron, so that the temperature is kept above the melting-point of steel during the whole of the operation. When the decarburation has been carried far enough, the current of air is stopped, and a small quantity of white pig iron, containing a large amount of manganese, is dropped into the liquid metal. This serves to facilitate the separation of any gas retained with the melted metal, which, after a few minutes' rest, is run into ingot moulds.

The most remarkable property of steel is that of becoming exceedingly hard when quickly cooled. When heated to redness, and suddenly quenched in cold water, steel, in fact, becomes capable of scratching glass with facility: if reheated to redness, and once more left to cool slowly, it again becomes nearly as soft as ordinary iron; and between these two conditions, any required degree of hardness may be attained. The articles, forged into shape, are first hardened in the manner described; they are then *tempered*, or *let down* by exposure to a proper degree of annealing heat, which is often judged of by the colour of the thin film of oxide which appears on the polished surface. Thus, a temperature of about 221° C. (430° F.), indicated by a faint straw colour, gives the proper temper for razors: that for scissors, penknives, &c., is comprised between 243° C. and 254° C. (470–490° F.), and is indicated by a full yellow or brown tint. Swords and watchsprings require to be softer and more elastic, and must be heated to 288° or 293° C. (550–560° F.), or until the surface becomes deep blue. Attention to these colours has now become of less importance, as metal baths are often substituted for the open fire in this operation.

NICKEL.

Atomic weight, 58·8. Symbol, Ni.

Nickel is found in tolerable abundance in some of the metal-bearing veins of the Saxon mountains, in Westphalia, Hessia, Hungary, and Sweden, chiefly as arsenide, the *kupfernickel* of mineralogists, so called from its yellowish-red colour. The word *nickel* is a term of detraction, having been applied by the old German miners to what was looked upon as a kind of false copper ore.

The artificial, or perhaps rather merely fused product, called *speiss*, is nearly the same substance, and may be employed as a source of the nickel salts. This metal is found in meteoric iron, as already mentioned.

Nickel is easily prepared by exposing the oxalate to a high white heat, in a crucible lined with charcoal, or by reducing one of the oxides by means of hydrogen at a high temperature. It is a white, malleable metal, having a density of 8·8, a high melting-point, and a less degree of oxidability than iron, since it is but little attacked by dilute acids. Nickel is strongly magnetic, but loses this property when heated to 350°.

Nickel Chloride, $NiCl_2$.—This compound is easily prepared by dissolving oxide or carbonate of nickel in hydrochloric acid. A green solution is obtained, which furnishes crystals of the same colour containing water. When rendered anhydrous by heat, the chloride is yellow, unless it contains cobalt, in which case it has a tint of green.

Nickel Oxides and **Oxysalts.**—Nickel forms two oxides analogous to the two principal oxides of iron.

The *monoxide*, NiO, is prepared by heating the nitrate to redness, or by precipitating a soluble nickel salt with caustic potash, and washing, drying, and igniting the apple-green hydrated oxide thrown down. It is an ashy-grey powder, freely soluble in acids, which it completely neutralises, forming salts isomorphous with those of magnesium and the other members of the same group. Nickel salts, when hydrated, have usually a beautiful emerald-green colour; in the anhydrous state they are yellow.

The *sesquioxide*, Ni_2O_3, is a black insoluble substance, prepared by passing chlorine through the hydrated monoxide suspended in water; nickel chloride is then formed, and the oxygen of the oxide decomposed is transferred to a second portion. It is also produced when a salt of nickel is mixed with a solution of bleaching-powder. The sesquioxide is decomposed by heat, and evolves chlorine when treated with hot hydrochloric acid.

NICKEL SULPHATE, $NiSO_4.7H_2O$.—This is the most important of the nickel salts. It forms green prismatic crystals, which require 3 parts of cold water for solution. Crystals with six molecules of water have also been obtained. It forms with the sulphates of potassium and ammonium beautiful double salts, $NiK_2(SO_4)_2.6H_2O$, and $Ni(NH_4)_2(SO_4)_2.6H_2O$, isomorphous with the corresponding magnesium salts.

When a strong solution of oxalic acid is mixed with sulphate of nickel, a pale bluish-green precipitate of oxalate falls after some time, very little nickel remaining in solution. The oxalate can thus be obtained for preparing the metal.

NICKEL CARBONATE, $NiCO_3$.—When solutions of nickel sulphate or chloride and of sodium carbonate are mixed, a pale-green precipitate falls, which is a combination of nickel carbonate and hydrate. It is readily decomposed by heat.

Pure nickel-salts are conveniently prepared on the small scale from crude speiss or kupfernickel by the following process:—The mineral is broken into small fragments, mixed with from one-fourth to half its weight of iron filings, and the whole dissolved in nitro-muriatic acid. The solution is gently evaporated to dryness, the residue treated with boiling water, and the insoluble iron arsenate removed by a filter. The liquid is then acidulated with hydrochloric acid, treated with hydrogen sulphide in excess, which precipitates the copper, and, after filtration, boiled with a little nitric acid to bring back the iron to the state of sesquioxide. To the cold and largely diluted liquid solution, acid sodium carbonate is gradually added, by which the ferric oxide may be completely separated without loss of nickel-salt. Lastly, the filtered solution, boiled with sodium carbonate in excess, yields an abundant pale green precipitate of nickel carbonate, from which all the other compounds may be prepared.

precipitated [illegible] [illegible] [illegible] left t
hours, and shaken up from time to t
is thereby thrown down as sesquioxid
solution, and may be precipitated a-
barium also contained in the solution
tation with sulphuric acid.*

Nickel-salts are well characterised b
Caustic alkalis give a pale apple-
insoluble in excess. *Ammonia* affor
is soluble in excess, with deep purplis
sodium carbonates give pale-green preci
a similar precipitate, soluble in excess
ferrocyanide gives a greenish-white p
produces a green precipitate, which
precipitant to an amber-coloured lic
addition of hydrochloric acid. *Hy*
change, if the nickel be in comb
Ammonium sulphide produces a black
which dissolves slightly in excess c
brown colour. Nickel sulphide when
in dilute hydrochloric acid; it is solu
nitric acid.

The chief use of nickel in the arts i
alloy, sometimes called German silv
100 parts of copper, 16 of zinc, and 40
malleable, and takes a high polish.

Another application, of recent int
deposition of nickel on iron, steel, co

COBALT.

Atomic weight, 58·8. Symbol, Co.

THIS substance bears, in many respects, a close resemblance to nickel: it is often associated with the latter in nature, and may be obtained from its compounds by similar means.

A cobalt salt free from nickel may be prepared by Rose's process just described. The precipitate, consisting of cobalt sesquioxide mixed with barium carbonate, is boiled with hydrochloric acid to reduce the cobalt sesquioxide to monoxide, and dissolve it as chloride together with the barium. The latter metal is then precipitated by sulphuric acid, and from the filtered liquid the cobalt may be precipitated as hydrate by potash. A solution of cobalt free from the nickel may also be obtained by precipitating the mixed solution with oxalic acid: the whole of the nickel is thereby precipitated, together with a small portion of the cobalt, leaving pure cobalt in solution.

Cobalt is a white, brittle, very tenacious metal, having a specific gravity of 8·5, and a very high melting point. It is unchanged in the air, and but feebly attacked by dilute hydrochloric and sulphuric acids. It is strongly magnetic.

Cobalt forms two classes of salts, analogous in composition to the ferrous and ferric salts; but the cobaltic salts, in which the metal is apparently trivalent, are very unstable.

Chlorides.—The *dichloride*, or *Cobaltous chloride*, $CoCl_2$, is easily prepared by dissolving the oxide in hydrochloric acid; or it may be prepared directly from *cobalt-glance*, the native arsenide, by a process exactly similar to that described in the case of nickel. It forms a deep rose-red solution, which, when sufficiently strong, deposits hydrated crystals of the same colour; when the liquid is evaporated by heat to a very small bulk, it deposits anhydrous crystals, which are blue: these latter by contact with water again dissolve to a red liquid. A dilute solution of cobalt chloride constitutes the well-known *blue sympathetic ink*: characters written on paper with this liquid are invisible, from their paleness of colour, until the salt has been rendered anhydrous by exposure to heat, when the letters appear blue. On laying it aside, moisture is absorbed, and the writing once more disappears. Green sympathetic ink is a mixture of the chlorides of cobalt and nickel.

The *trichloride*, or *Cobaltic chloride*, Co_2Cl_6, is obtained in solution by dissolving the sesquioxide in hydrochloric acid, and in small quantity by saturating a solution of the dichloride with chlorine gas. The liquid has a dark-brown colour, but easily decomposes, giving off chlorine and leaving the rose-coloured dichloride.

Oxides and **Oxysalts.**—Cobalt forms two oxides analogous to those of nickel, also two or three of intermediate composition, but not very well defined. The *monoxide*, or *cobaltous oxide*, CoO, is a grey powder, very soluble in acids, and is a strong base, isomorphous with magnesia, affording salts of a fine red tint. It is prepared by precipitating cobaltous sulphate or chloride with sodium carbonate, and washing, drying, and igniting the precipitate. When the cobalt solution is mixed with caustic potash, a beautiful blue precipitate falls, which, when heated, becomes violet, and at length dirty red, from absorption of oxygen and a change in the state of hydration.

The *sesquioxide*, or *Cobaltic oxide*, Co_2O_3, is a black, insoluble, neutral powder, obtained by mixing solutions of cobalt and chloride of lime. It dissolves in acids, yielding the cobaltic salts.

Cobaltoso-cobaltic oxide, Co_3O_4, analogous to the magnetic oxide of iron, is formed when cobaltous nitrate or oxalate, or hydrated cobaltic oxide, is heated in contact with the air. According to Frémy, it is a salifiable base.

Another oxide, of acid character, is said to be obtained, in the form of a potassium salt, by fusing the monoxide or sesquioxide with potassium hydroxide. A crystalline salt is thus formed, consisting, according to Schwarzenberg, of $K_2O.3Co_3O_4.3$ aq.

COBALTOUS SULPHATE, $CoSO_4.7H_2O$.—This salt forms red crystals, requiring for solution 24 parts of cold water: they are identical in form with those of magnesium sulphate. It combines with the sulphates of potassium and ammonium, forming double salts, which contain, as usual, 6 molecules of water.

A solution of oxalic acid added to cobaltous sulphate occasions, after some time, the separation of nearly the whole of the base in the state of oxalate.

COBALTOUS CARBONATE.—The alkaline carbonates produce in solutions of cobalt a pale peach-blossom-coloured precipitate of combined carbonate and hydrate, containing $2CoCO_3.3CoH_2O_2 +$ aq.

Ammoniacal Cobalt compounds.—Cobaltous salts, treated with ammonia in a vessel protected from the air, unite with the ammonia, forming compounds which may be called ammonio-cobaltous salts. Most of them contain 6 molecules of ammonia to 1 molecule of the cobalt-salt; thus the chloride contains $CoCl_2.6NH_3$.aq.; the nitrate, $Co(NO_3)_2 6NH_3$.2 aq. They are generally crystallisable, and of a rose-colour, soluble without decomposition in ammonia, but decomposed by water, with formation of a basic salt. H. Rose, by treating dry cobalt chloride with ammonia gas, obtained the compound $CoCl_2.4NH_3$; and in like manner an ammonio-sulphate has been formed containing $CoSO_4.6NH_3$.

When an ammoniacal solution of cobalt is exposed to the air, oxygen is absorbed, the liquid turns brown, and new salts are formed, containing a higher oxide of cobalt (either Co_2O_3, or CoO_2), and therefore designated generally as peroxidised ammonio-cobalt salts. Several of them, containing different bases, are often formed at the same time. Most of the peroxidised ammonio-cobalt salts are composed of cobaltic salts united with two or more molecules of ammonia. The composition of the normal salts may be illustrated by the chlorides, as in the following table :—

Tetrammonio-cobaltic chloride, . . .	$Co_2Cl_6 . 4NH_3$
Hexammonio-cobaltic chloride, . . .	$Co_2Cl_6 . 6NH_3$
Octammonio-cobaltic (or fusco-cobaltic) chloride, ...	$Co_2Cl_6 . 8NH_3$
Decammonio-cobaltic (roseo- and purpureo-cobaltic) chloride, . . .	$Co_2Cl_6 . 10NH_3$
Dodecammonio-cobaltic (or luteo-cobaltic) chloride, ...	$Co_2Cl_6 . 12NH_3$.

The formulæ of the corresponding normal nitrates are deduced from the preceding by substituting NO_3 for Cl ; those of the sulphates, oxalates, and other bibasic salts, by substituting SO_4, C_2O_4, &c., for Cl_2. Thus *decammonio-cobaltic sulphate*$=Co_2(SO_4)_3.10NH_3$. There are also several acid and basic salts of the same ammonia-molecules. Further, there is a class of salts containing the elements of nitrogen dioxide or nitrosyl, NO, in addition to ammonia, *e.g.*, *decammonio-nitroso-cobaltic* or *xantho-cobaltic oxychloride*, $Co_2Cl_4O.10NH_3.N_2O_2$. Lastly, Frémy has obtained ammoniacal compounds (*oxycobaltic salts*) containing salts of cobalt corresponding with the dioxide.*

Cobaltous salts have the following characters :—

Solution of *potash* gives a blue precipitate, changing by heat to violet and red. *Ammonia* gives a blue precipitate, soluble with difficulty in excess, with brownish-red colour. *Sodium carbonate* forms a pink precipitate. *Ammonium carbonate*, a similar compound, soluble in excess. *Potassium ferrocyanide* gives a greyish-green precipitate. *Potassium cyanide* forms a yellowish-brown precipitate, which dissolves in an excess of the precipitant. The clear solution, after boiling, may be mixed with hydrochloric acid without giving a precipitate. *Hydrogen sulphide* produces no change, if the cobalt is combined with a strong acid. *Ammonium sulphide* throws down black sulphide of cobalt, insoluble in dilute hydrochloric acid.

Cobaltic salts, formed by disssolving cobaltic oxide in acids, give, with *potash*, a dark-brown precipitate of hydrated cobaltic oxide ; with ammonia, a brownish-red solution; with the *fixed alkaline carbonates*, a green solution, which deposits a small quantity of cobaltic oxide; with *ammonium sulphide* (after saturation of the free acid by ammonia), a black precipitate.

* For the preparation and properties of all these salts, see Watts's Dictionary of Chemistry, vol. i. 1051, first Supplement, p. 479, and second Supplement, p. 363. Their rational formulæ are similar to those of the ammoniacal platinum salts (p. 512).

The substance called *smalt*, use
coloured by cobalt : it is thus m
until nearly free from arsenic, an
potassium carbonate and quartz-san
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powder and elutriated. *Cobalt ultr*
pared by mixing 16 parts of freshly
of cobalt phosphate or arsenate : t
heated to redness. By daylight th
artificial light it is violet. A sim
colour, is formed by igniting zinc ox
the roasted cobalt ore mixed with sil
powder : it is used in enamel painti
tions of the oxides of cobalt, mangan
a fine black colour to glass.

MANGAN

Atomic weight, 55.

MANGANESE is tolerably abundant i
forming, or entering into the com
minerals. Traces of this substance a
ashes of plants.
Metallic manganese, or perhaps

the crucible is broken up, and the metallic button of manganese extracted.

Deville has lately prepared pure manganese by reducing pure manganese oxide with an insufficient quantity of sugar charcoal in a crucible made of caustic lime. Thus prepared, metallic manganese possesses a reddish lustre like bismuth : it is very hard and brittle, and, when powdered, decomposes water, even at the lowest temperature. Dilute sulphuric acid dissolves it with great energy, evolving hydrogen. Brunner produced metallic manganese from manganese and sodium fluoride by means of sodium. The metal obtained by this process scratches glass and hardened steel, and has a specific gravity of 7·13.

Manganese is usually regarded as a metal of the iron group, inasmuch as it forms a dichloride and trichloride analogous to the iron chlorides, together with oxides and other compounds of corresponding constitution. On the other hand, it is said to form a heptachloride, $MnCl_7$, according to which it should be regarded as a heptad ; and it exhibits the same degree of quantivalence in the permanganates (pp. 267, 507).

Manganese Chlorides.—The *dichloride*, or *Manganous chloride*, may be prepared in a state of purity from the dark brown liquid residue of the preparation of chlorine from manganese dioxide and hydrochloric acid, which often accumulates in the laboratory to a considerable extent in the course of investigation : from the pure chloride, the carbonate and all the other salts can be conveniently obtained. The liquid referred to consists chiefly of the mixed chlorides of manganese and iron : it is filtered, evaporated to perfect dryness, and the residue is slowly heated to dull ignition in an earthen vessel, with constant stirring. The iron chloride is thus either volatilised, or converted by the remaining water into insoluble sesquioxide, while the manganese salt is unaffected. On treating the greyish-looking powder thus obtained with water, the manganese chloride is dissolved out, and may be separated by filtration from the iron oxide. Should a trace of the latter yet remain, it may be got rid of by boiling the liquid for a few minutes with a little manganese carbonate. The solution of the chloride has usually a delicate pink colour, which becomes very manifest when the salt is evaporated to dryness. A strong solution deposits rose-coloured tabular crystals, which contain 4 molecules of water ; they are very soluble and deliquescent. The chloride is fusible at a red-heat, is decomposed slightly at that temperature by contact with air, and is dissolved by alcohol, with which it forms a crystallisable compound.

The *trichloride*, or *Manganic chloride*, Mn_2Cl_6, is formed when precipitated manganic oxide is immersed in cold concentrated hydrochloric acid, the oxide then dissolving quietly without evolution of gas. Heat decomposes the trichloride into dichloride and free chlorine.

Heptachloride, $MnCl_7$ (?).—When potassium permanganate is dissolved in strong sulphuric acid, and fused sodium chloride is added by small portions at a time, a greenish-yellow gas is given off, which condenses at 0° to a greenish-brown liquid. This compound, when exposed to moist air, gives off fumes, coloured purple by permanganic acid, and is instantly decomposed by water into permanganic and hydrochloric acids. It is regarded by Dumas, who discovered it, as the heptachloride of manganese; but H. Rose regarded it as an oxychloride, $MnCl_2O_2$, analogous to chromic oxychloride, a view which is in accordance with its mode of formation.

Fluorides of manganese have been formed analogous to each of these chlorides.

Manganese Oxides and **Oxysalts.**—Manganese forms four well-defined oxides, constituted as follows:—

Monoxide, or Manganous oxide,	MnO
Trimangano-tetroxide, or Manganoso-manganic oxide,	Mn_3O_4
Sesquioxide, or Manganic oxide,	Mn_2O_3
Dioxide or Peroxide,	MnO_2.

The first is a strong base, the third a weak base; the second and fourth are neutral; the second may be regarded as a compound of the first and third, $MnO.Mn_2O_3$. There are also several oxides intermediate between the monoxide and dioxide, occurring as natural minerals or ores of manganese. Manganese likewise forms two series of oxygen-salts, called *manganates* and *permanganates*, the composition of which may be illustrated by the potassium salts, viz.:

Potassium manganate,	$K_2MnO_4 = K_2O.MnO_3$
Potassium permanganate,	$K_2Mn_2O_8 = K_2O.Mn_2O_7$.

The oxides, MnO_3 and Mn_2O_7, corresponding with these salts, are not known.

Monoxide, or *Manganous oxide*, MnO.—When manganese carbonate is heated in a stream of hydrogen gas, or vapour of water, carbon dioxide is disengaged, and a greenish powder left behind, which is the monoxide. Prepared at a dull red heat only, the monoxide is so prone to absorb oxygen from the air, that it cannot be removed from the tube without change; but when prepared at a higher temperature, it appears more stable. This oxide is a very powerful base, being isomorphous with magnesia and zinc oxide; it dissolves quietly in dilute acids, neutralising them completely, and forming salts, which have often a beautiful pink colour. When alkalis are added to solutions of these compounds, the white hydrated oxide first precipitated speedily becomes brown by passing into a higher state of oxidation.

Sesquioxide, or *Manganic oxide*, Mn_2O_3.—This compound occurs in nature as *braunite*, and in the state of hydrate as *manganite*: a very beautiful crystallised variety is found at Ilefeld, in the Hartz. It is produced artificially, by exposing the hydrated monoxide to the air, and forms the principal part of the residue left in the iron retort when oxygen gas is prepared by exposing the native dioxide to a moderate red-heat. The colour of the sesquioxide is brown or black, according to its origin or mode of preparation. It is a feeble base, isomorphous with alumina: for when gently heated with diluted sulphuric acid, it dissolves to a red liquid, which, on the addition of potassium or ammonium sulphate, deposits octohedral crystals, having a constitution similar to that of common alum: these are, however, decomposed by water. Strong nitric acid resolves this oxide into a mixture of monoxide and dioxide, the former dissolving, and the latter remaining unaltered: while hot oil of vitriol destroys it by forming manganous sulphate and liberating oxygen gas. On heating it with hydrochloric acid, chlorine is evolved, as with the dioxide, but in smaller amount.

Dioxide, MnO_2.—*Peroxide of Manganese. Pyrolusite.*—The most common ore of manganese; it is found both massive and crystallised. It may be obtained artificially in the anhydrous state by gently calcining the nitrate, or in combination with water, by adding solution of bleaching powder to a salt of the monoxide. Manganese dioxide has a black colour, is insoluble in water, and refuses to unite with acids. It is decomposed by hot hydrochloric acid and by oil of vitriol in the same manner as the sesquioxide. It unites with the stronger bases, potash, lime, &c., forming salts called manganites, *e.g.*, $CaO.MnO_2$ or $CaMnO_3$, which are produced by precipitating a solution of a manganous salt with the corresponding base in presence of an oxidising agent, such as a stream of air or oxygen gas. Such are the manganites of calcium and magnesium formed in Weldon's process for the recovery of manganese dioxide from waste chlorine-liquors (p. 187). According to Frémy,* manganese dioxide likewise acts as a base, forming definite salts with acids, *e.g.*, a sulphate, $MnO_2.SO_3$.

The proportion of real dioxide contained in a commercial sample of the black oxide may be determined as follows:—50 grains of the mineral, reduced to very fine powder, are put into the little vessel employed in the analysis of carbonates (p. 352), together with about half an ounce of cold water, and 100 grains of strong hydrochloric acid; 50 grains of crystallised oxalic acid, $C_2H_2O_4$, are then added, the cork carrying the drying tube is fitted, and the whole quickly weighed or counterpoised. The application of a gentle heat suffices to determine the action; the oxalic acid is oxidised into water and carbon dioxide, which escapes as gas, while the manganese remains in solution as manganous chloride:

$$MnO_2 + C_2H_2O_4 + 2HCl = MnCl_2 + 2H_2O + 2CO_2.$$

This equation shows that every two molecules of carbon dioxide evolved correspond with one molecule of manganese dioxide decomposed. Now the molecular weight of this oxide, 87, is so nearly equal to twice that of carbon dioxide, 44, that the loss of weight suffered by the apparatus when the reaction has become complete, and the residual gas has been driven off by momentary ebullition, may be taken to represent the quantity of real dioxide in the 50 grains of the sample. The apparatus of Will and Fresenius, described at page 353, may also be used with advantage in this process.

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* Comptes Rendus, lxxxii. 1231; Chem. Soc. Journal, 1877, i. 52.

Trimangano-tetroxide, or *Red manganese oxide*, Mn_3O_4, or probably $MnO.Mn_2O_3$.—This oxide is also found native, as *hausmannite*, and is produced artificially by heating the dioxide or sesquioxide to whiteness, or by exposing the monoxide or carbonate to a red heat in an open vessel. It is a reddish-brown substance, incapable of forming salts, and acted upon by acids in the same manner as the two other oxides already described. Borax and glass in the fused state dissolve it, and acquire the colour of the amethyst.

Varvicite, $Mn_4O_7.H_2O$ or $MnO.3MnO_2.H_2O$, is a natural mineral, discovered by Phillips among certain specimens of manganese ore from Warwickshire: it has also been found at Ilefeld in the Hartz. It much resembles the dioxide, but is harder and more brilliant. By a strong heat, varvicite is converted into red oxide, with disengagement of aqueous vapour and oxygen gas.

Several other oxides, intermediate in composition between the monoxide and dioxide, also occur native; they are probably mere mixtures, and in many cases the monoxide is more or less replaced by the corresponding oxides of iron, cobalt, and copper.

MANGANOUS SULPHATE, $MnSO_4.7H_2O$ or $MnO.SO_3.7H_2O$.—A beautiful rose-coloured and very soluble salt, isomorphous with magnesium sulphate. It is prepared on the large scale for the use of the dyer, by heating in a close vessel manganese dioxide and coal, and dissolving the impure monoxide thus obtained in sulphuric acid, with addition of a little hydrochloric acid towards the end of the process. The solution is evaporated to dryness, and again exposed to a red heat, by which ferric sulphate is decomposed. Water then dissolves out the pure manganese sulphate, leaving ferric oxide behind. The salt is used to produce a permanent brown dye, the cloth steeped in the solution being afterwards passed through a solution of bleaching powder, by which the monoxide is changed to insoluble hydrate of the dioxide. Manganous sulphate sometimes crystallises with 5 molecules of water. It forms a double salt with potassium sulphate, containing $MnK_2(SO_4)_2.6H_2O$.

MANGANOUS CARBONATE, $MnCO_3$ or $MnO.CO_2$.—Prepared by precipitating the dichloride with an alkaline carbonate. It is an insoluble white powder, sometimes with a buff-coloured tint. Exposed to heat, it loses carbon dioxide and absorbs oxygen.

MANGANATES.—When an oxide of manganese is fused with potash, oxygen is taken up from the air, and a deep green saline mass results, which contains *potassium manganate*, K_2MnO_4 or $K_2O.MnO_3$. The addition of potassium nitrate or chlorate facilitates the reaction. Water dissolves this compound very readily, and the solution, concentrated by evaporation in a vacuum, yields green crystals. *Barium manganate*, $BaMnO_4$, is formed in a similar manner. In these salts manganese is sexvalent, like chromium in the chromates.

PERMANGANATES.—When potassium manganate, free from any great excess of alkali, is put into a large quantity of water, it is resolved into hydrated manganese dioxide, which subsides, and *potassium permanganate*, $K_2Mn_2O_8$ or $K_2O.Mn_2O_7$, which remains in solution, forming a deep purple liquid :

$$3K_2MnO_4 + 2H_2O = MnO_2 + K_2Mn_2O_8 + 4KHO.$$

This effect is accelerated by heat. The changes of colour accompanying this decomposition are very remarkable, and have procured for the manganate the name *mineral chameleon ;* excess of alkali hinders the reaction in some measure, by conferring greater stability on the manganate. Potassium permanganate is easily prepared on a considerable scale. Equal parts of very finely powdered manganese dioxide and potassium chlorate are mixed with rather more than one part of potassium hydroxide dissolved in a little water, and the whole is exposed, after evaporation to dryness, to a temperature just short of ignition. The mass is treated with hot water, the insoluble oxide separated by decantation, and the deep-purple liquid concentrated by heat, until crystals form upon its surface : it is then left to cool. The crystals have a dark purple colour, and are not very soluble in cold water. The manganates and permanganates are decomposed by contact with organic matter : the former are said to be isomorphous with the sulphates, and the latter with the perchlorates. The green and red disinfecting agents, known as Condy's fluids, are alkaline manganates and permanganates.

Hydrogen permanganate, or *Permanganic acid*, $H_2Mn_2O_8$, is obtained by dissolving potassium permanganate in hydrogen sulphate, H_2SO_4, diluted with one molecule of water, and distilling the solution at 60°–70°. Permanganic acid then passes over in violet vapours, and condenses to a greenish-black liquid, which has a metallic lustre, absorbs moisture greedily from the air, and acts as a most powerful oxidising agent, instantly setting fire to paper and to alcohol. In this acid and its salts the manganese is septivalent (p. 267).

Manganous salts are very easily distinguished by reagents. The *fixed caustic alkalis* and *ammonia* give white precipitates, insoluble in excess, quickly becoming brown. The *carbonates of the fixed alkalis* and *carbonate of ammonia* give white precipitates, but little subject to change, and insoluble in excess of carbonate of ammonia. *Hydrogen sulphide* gives no precipitate, but *ammonium sulphide* throws down insoluble flesh-coloured sulphide of manganese, which is very characteristic. *Potassium ferrocyanide* gives a white precipitate.

Manganese is also easily detected by the blowpipe: it gives with borax an amethyst-coloured bead in the outer or oxidising flame, and a colourless one in the inner flame. Heated upon platinum foil with sodium carbonate, it yields a green mass of sodium manganate.

CLASS VIII.—GROUP II.—PLATINUM METALS.

PLATINUM.

Atomic weight, 197·6. Symbol, Pt.

PLATINUM, palladium, rhodium, iridium, ruthenium, and osmium, form a group of metals, allied in some cases by properties in common, and still more closely by their natural association. *Crude platinum*, a native alloy of platinum, palladium, rhodium, iridium, and a little iron, occurs in grains and rolled masses, sometimes of tolerably large dimensions, mixed with gravel and transported materials, on the slope of the Ural Mountains in Russia, also in Brazil, Ceylon, and a few other places. It has never been seen in the rock, which, however, is judged from the accompanying materials to have been serpentine. It is stated to be always present in small quantities with native silver.

From this substance platinum is prepared by the following process :—The crude metal is acted upon as far as possible by nitromuriatic acid containing an excess of hydrochloric acid and slightly diluted with water, in order to dissolve as small a quantity of iridium as possible : to the deep yellowish red and highly acid solution thus produced, sal-ammoniac is added, by which nearly the whole of the platinum is thrown down in the state of ammonium platinochloride. This substance, washed with a little cold water, dried, and heated to redness, leaves metallic platinum in the spongy state. This metal cannot be fused into a compact mass by ordinary furnace-heat, but the same object may be accomplished by taking advantage of its property of welding, like iron, at a high temperature. The spongy platinum is made into a thin uniform paste with water, introduced into a slightly conical mould of brass, and subjected to a graduated pressure, by which the water is squeezed out, and the mass rendered at length sufficiently solid to bear handling. It is then dried, very carefully heated to whiteness, and hammered, or subjected to powerful pressure. If this operation is properly conducted, the platinum will then be in a state to bear forging into a bar, which can afterwards be rolled into plates, or drawn into wire at pleasure.

A method of refining platinum has lately been devised by Deville and Debray. It consists in submitting the crude metal to the action of an intensely high temperature in a crucible of lime. The apparatus they employ is as follows :—The lower part of the furnace consists of a piece of lime, hollowed out in the centre to the depth of about a quarter of an inch ; a small notch is filed at one side of this basin, through which the metal is introduced and poured out. A cover made of another piece of lime fits on the top of this basin; it is also hollowed to a small extent, and has a conical perforation at the top, into which is inserted the nozzle of an oxy-hydrogen blowpipe. The whole arrangement is firmly bound with iron wire. To use the apparatus, the stopcock supplying the hydrogen (or coal gas) is opened, and the gas lighted at the notch in the crucible: the oxygen is then gradually supplied; and when the furnace is sufficiently hot, the metal is introduced in small pieces through the orifice. By this arrangement as much as 50 pounds of platinum and more may be fused at once. All the impurities in the platinum, except the iridium and rhodium, are separated in this manner: the gold and palladium are volatilised; the sulphur, phosphorus, arsenic, and osmium oxidised and volatilised; and the iron and copper oxidised and absorbed by the lime of the crucible.

Platinum is a little whiter than iron: it is exceedingly malleable and ductile, both hot and cold, and is very infusible, melting only before the oxy-hydrogen blowpipe, or in the powerful blast furnace just described. It is the heaviest substance known, its specific gravity being 21·5. Neither air, moisture, nor the ordinary acids attack platinum in the slightest degree at any temperature: hence its great value in the construction of chemical vessels. It is dissolved by nitro-muriatic acid, and superficially oxidised by fused potassium hydroxide, which enters into combination with the oxide.

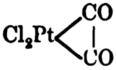
The remarkable property of the spongy metal to determine the union of oxygen and hydrogen has been already noticed. There is a still more curious state in which platinum can be obtained—that of *platinum-black*, in which the division is carried much further. It is easily prepared by boiling a solution of platinic chloride to which an excess of sodium carbonate and a quantity of sugar have been added, until the precipitate formed after a little time becomes perfectly black, and the supernatant liquid colourless. The black powder is collected on a filter, washed, and dried by gentle heat. This substance appears to possess the property of condensing gases, more especially oxygen, into its pores to a very great extent: when placed in contact with a solution of formic acid, it converts the latter, with copious effervescence, into carbonic acid; alcohol, dropped upon the platinum-black, becomes changed by oxidation to acetic acid, the rise of temperature being often sufficiently great to cause inflammation. When exposed to a red heat, the black substance shrinks in volume, assumes the appearance of common spongy platinum, and loses these peculiarities, which are no doubt the result of its excessively comminuted state.

Platinum forms two series of compounds: the platinous compounds, in which it is bivalent, *e.g.*, $PtCl_2$, PtO, and the platinic compounds, in which it is quadrivalent, *e.g.*, $PtCl_4$, PtO_2, &c.

Chlorides.—The *dichloride*, or *Platinous chloride*, $PtCl_2$, is produced when platinic chloride, dried and powdered, is exposed for [illegible] crystals, containing, n corresponding sodium compound to crystallise. These double salts *chloroplatinites*. Platinous chloric chlorine and metallic platinum.

Platinous chloride unites with three compounds

$$Cl_2Pt{=}CO\,,$$



$$Cl_2Pt\langle CO\,|\,CO$$

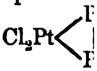
all of which are produced by heating of carbon monoxide. The first ai needles, the second in white needles.

Platinous chloride also unites with ing phospho-platinic chloride, (by heating spongy platinum with ph It crystallises in maroon-coloured ne heated with excess of phosphorus tri

diphosphoplatinic chloride, Cl_2l

yellow crystals, melting at 160°. The by water—the latter on exposure t temperature—into phosphoplatini

acids, $Cl_2Pt{=}P(OH)_3$ and



tribasic, the latter sexbasic.

Platinum tetrachloride, or *Platinic c* when platinum is heat. It is easily reduced by hydrogen at a high temperature, yielding a mixture of potassium chloride and platinum-black: the latter substance may thus, indeed, be very easily prepared. The *sodium salt*, $2NaCl.PtCl_4,6H_2O$, is very soluble, crystallising in large, transparent, yellow-red prisms of great beauty. The *ammonium salt*, $2NH_4Cl.PtCl_4$, is undistinguishable, in physical characters, from the potassium-salt: it is thrown down as a precipitate of small, transparent, yellow, octohedral crystals when sal-ammoniac is mixed with platinic chloride; it is but feebly soluble in water, still less so in dilute alcohol, and is decomposed by heat, yielding spongy platinum, while sal-ammoniac, hydrochloric acid, and nitrogen are driven off. Platinic chloride also forms crystallisable double salts with the hydrochlorides of many organic bases; with ethylamine, for example, the compound, $2[NH_2(C_2H_5).HCl]_2PtCl_4$.

The *bromides* and *iodides of platinum* are analogous in composition to the *chlorides*, and likewise form double salts with alkaline bromides and iodides.

Oxides.—The *monoxide*, or *Platinous oxide*, PtO, is obtained by digesting the dichloride with caustic potash, as a black powder, soluble in excess of alkali. It dissolves also in acids with brown colour, and the solutions are not precipitated by sal-ammoniac. When platinum dioxide is heated with solution of oxalic acid, it is reduced to monoxide, which remains dissolved. The liquid has a dark blue colour, and deposits fine copper-red needles of platinous oxalate.

The *dioxide*, or *Platinic oxide*, PtO_2, is best prepared by adding barium nitrate to a solution of platinic sulphate; barium sulphate and platinic nitrate are then produced, and from the latter caustic soda precipitates one-half of the platinum as *platinic hydrate*. The sulphate is itself obtained by acting with strong nitric acid upon platinum bisulphide, which falls as a black powder when a solution of the tetrachloride is dropped into potassium sulphide. Platinic hydrate is a bulky brown powder, which, when gently heated, becomes black and anhydrous. It may also be formed by boiling platinic chloride with a great excess of caustic soda, and then adding acetic acid. It dissolves in acids, and combines with bases: the salts have a yellow or red tint, and a great disposition to unite with salts of the alkalis and alkaline earths, giving rise to a series of double compounds, which are not precipitated by excess of alkali. A combination of platinic oxide with ammonia exists, which is explosive. Both oxides of platinum are reduced to the metallic state by ignition.

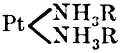
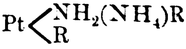
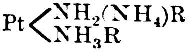
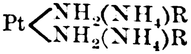
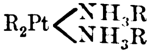
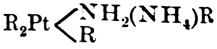
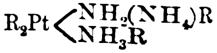
Sulphides.—The compounds, PtS and PtS_2, are produced by the action of hydrogen sulphide, or the hydrosulphide of an alkali-metal, on the dichloride and tetrachloride of platinum respectively; they are both black substances, insoluble in water. Platinic sulphide heated in a close vessel gives off half its sulphur, and is reduced to platinous sulphide. It dissolves in alkaline hydrates, carbonates, and sulphides, forming salts called *sulphoplatinates*, which are decomposed by acids.

Ammoniacal Platinum Compounds.—The chlorides, oxides, sulphates, &c., of platinum are capable of taking up two or more molecules of ammonia, and forming compounds analogous in many respects to the ammoniacal mercury compounds already described.

The nitrogen in all these compounds is quinquivalent, and consequently the groups *ammonia*, NH_3, and *diammonia* N_2H_6 or NH_3—NH_3 or $NH_2(NH_4)$, are bivalent, having two free combining units.

The platinum in some of these compounds is bivalent (*plato* or *platoso*), and unites by two of its combining units with the bivalent groups NH_3 or N_2H_6, each of which retains one combining unit free. In others the platinum is quadrivalent (*platino*), and unites by some of its combining units with ammonia or diammonia, the remaining units being satisfied by combination with electro-negative radicles. In others, again, the platinum accumulates in such a manner as to form compounds containing $(Pt_2)''$, $(Pt^{iv}—Pt^{iv})^{vi}$, $(Pt^{iv}—Pt^{iv}—Pt^{iv}—Pt^{iv})^{x}$, &c. The bivalent groups, NH_3, N_2H_6, always go by pairs, excepting in the semi-diammoniums, in which half or a quarter of the combining units of the platinum is satisfied by one N_2H_6.

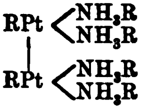
The names and constitution of the several groups are given in the following table, the symbol R denoting a univalent chlorous radicle, such as Cl, NO_2 &c.

1. Platosammonium compounds,	 $Pt\left\langle\begin{matrix}NH_3R\\NH_3R\end{matrix}\right.$
2. Platosemidiammonium compounds,	 $Pt\left\langle\begin{matrix}NH_2(NH_4)R\\R\end{matrix}\right.$
3. Platomonodiammonium compounds,	 $Pt\left\langle\begin{matrix}NH_2(NH_4)R\\NH_3R\end{matrix}\right.$
4. Platosodiammonium compounds,	 $Pt\left\langle\begin{matrix}NH_2(NH_4)R\\NH_2(NH_4)R\end{matrix}\right.$
5. Platinammonium compounds,	 $R_2Pt\left\langle\begin{matrix}NH_3R\\NH_3R\end{matrix}\right.$
6. Platinosemidiammonium compounds,	 $R_2Pt\left\langle\begin{matrix}NH_2(NH_4)R\\R\end{matrix}\right.$
7. Platinomonodiammonium compounds,	 $R_2Pt\left\langle\begin{matrix}NH_2(NH_4)R\\NH_3R\end{matrix}\right.$

8. Platinodiammonium compounds,

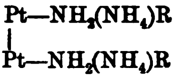
$$\mathrm{R_2Pt}\Big<\begin{matrix}\mathrm{NH_2(NH_4)R}\\ \mathrm{NH_2(NH_4)R}\end{matrix}$$

9. Diplatinammonium compounds,



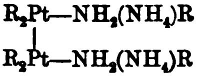
$$\begin{array}{l}\mathrm{RPt}\Big<\begin{matrix}\mathrm{NH_3R}\\ \mathrm{NH_3R}\end{matrix}\\ \quad|\\ \mathrm{RPt}\Big<\begin{matrix}\mathrm{NH_3R}\\ \mathrm{NH_3R}\end{matrix}\end{array}$$

10. Diplatosodiammonium compounds,



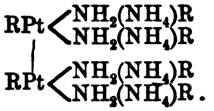
$$\begin{array}{l}\mathrm{Pt{-}NH_2(NH_4)R}\\ |\\ \mathrm{Pt{-}NH_2(NH_4)R}\end{array}$$

11. Diplatinodiammonium compounds,



$$\begin{array}{l}\mathrm{R_2Pt{-}NH_2(NH_4)R}\\ \quad|\\ \mathrm{R_2Pt{-}NH_2(NH_4)R}\end{array}$$

12. Diplatinotetradiammonium compounds,



$$\begin{array}{l}\mathrm{RPt}\Big<\begin{matrix}\mathrm{NH_2(NH_4)R}\\ \mathrm{NH_2(NH_4)R}\end{matrix}\\ \quad|\\ \mathrm{RPt}\Big<\begin{matrix}\mathrm{NH_2(NH_4)R}\\ \mathrm{NH_2(NH_4)R}\end{matrix}.\end{array}$$

We shall here describe the most characteristic compounds of each group, referring for more complete description to larger works.*

1. *Platosammonium Compounds.*—These compounds are formed by abstraction of the elements of ammonia, NH_3, from the corresponding platosodiammonium-compounds. They are for the most part insoluble in water, but dissolve in ammonia, reproducing the platosodiammonium-compounds. They detonate when heated.

The *chloride*, $\mathrm{Pt}\Big<\begin{matrix}\mathrm{NH_3Cl}\\ \mathrm{NH_3Cl}\end{matrix}$ or $N_2H_6PtCl_2$, is formed by heating platosodiammonium chloride to 220°–270°, or by heating the same salt with hydrochloric acid, or by boiling the green salt of Magnus (p. 515) with nitrate or sulphate of ammonium, and is deposited as a yellow crystalline powder, or in rhombohedral scales. It dissolves in 4472 parts of water at 0° and in 130 parts of boiling water. At 270° it decomposes in the manner represented by the equation,

$$3N_2H_6PtCl_2 = 3Pt + 4NH_4Cl + 2HCl + N_2.$$

Silver nitrate added to its solution throws down all the chlorine. This salt is isomeric with the green salt of Magnus, with the yellow chloride of platosemidiammonium, and with the chloroplatinite of platosomonodiammonium.

The corresponding *iodide*, $N_2H_6PtI_2$, is a yellow powder, obtained by heating the aqueous solution of the compound, $N_4H_{12}PtI_2$. It dissolves in ammonia, reproducing the latter compound. The *oxide*,

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* See Watts's Dictionary of Chemistry, iv. 673, and 2d Suppl. 992.

N_2H_6PtO, obtained by heating platosodiammonium oxide (p. 515) to 110°, is a greyish mass, which, when heated to 100° in a close vessel, gives off water, ammonia, and nitrogen, and leaves metallic platinum. The *hydroxide*, $N_2H_6Pt.(HO)_2$, obtained by decomposing the sulphate with baryta-water, is a strong base, soluble in water, having an alkaline reaction, absorbing carbonic acid from the air, and liberating ammonia from its salts (Odling). The *sulphate*, $N_2H_6PtSO_4.H_2O$, and the *nitrate*, $N_2H_6Pt(NO_3)_2$, are obtained by boiling the iodide with sulphate and nitrate of silver : they are crystalline, and have a strong acid reaction. The sulphate retains a molecule of crystallisation-water, which cannot be removed without decomposing the salt.

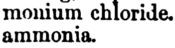
2. *Platososemidiammonium Compounds.*—These compounds, isomeric with the preceding, are formed by direct addition of ammonia to platinous salts. The *chloride*, $\mathrm{Pt}\left\langle\begin{matrix}\mathrm{N_2H_6Cl}\\ \mathrm{Cl}\end{matrix}\right.$, is obtained by adding ammonia to a cold solution of platinous chloride in hydrochloric acid, filtering after 24 hours, and treating the yellowish green residue with boiling water, which dissolves the platosemidiammonium salt, and leaves the green salt of Magnus formed at the same time. The solution on cooling deposits the platososemidiammonium chloride in small prisms, differing in form from the chloride above described, and much more soluble in water, requiring for solution 387 parts of cold and 26 parts of boiling water. The other salts of this base are obtained by decomposing the chloride with the corresponding silver salts. The *bromide* and *iodide* crystallise in yellow needles; the *nitrite* in silky needles, which detonate when heated; the *nitrate* and *sulphate* form yellowish crystalline crusts.

3. *Platosomonodiammonium Compounds*, $\mathrm{Pt}\left\langle\begin{matrix}\mathrm{N_2H_6R}\\ \mathrm{NH_3R}\end{matrix}\right.$.—The *chloroplatinite* of this series, $2N_3H_9PtCl_2.PtCl_2$, formed in small quantity on adding ammonia to a solution of platinous chloride, crystallises in brown square laminæ, slightly soluble in cold, more soluble in boiling water. Treated with silver nitrate it is converted into platosomonodiammonium *nitrate*, and this, when heated with hydrochloric acid, yields the corresponding *chloride*, $N_3H_9PtCl_2$, which is very soluble, and crystallises in colourless needles, or nacreous scales.

4. *Platosodiammonium Compounds*, $\mathrm{Pt}\left\langle\begin{matrix}\mathrm{N_2H_6R}\\ \mathrm{N_2H_6R}\end{matrix}\right.$.—The *chloride*, $N_4H_{12}PtCl_2$, one of the earliest discovered of the ammoniacal platinum compounds, is obtained by the action of ammonia on the green salt of Magnus, or on the chloride of platosammonium. When platinous chloride is boiled with excess of ammonia, till the green precipitate formed in the first instance is redissolved, a solution is obtained, which, when filtered and evaporated, yields the chloride of platosodiammonium in splendid yellow crystals containing one molecule of water, which they give off at 110°. It is soluble in water, and its solution mixed with platinous chloride

yields *platosodiammonium chloroplatinite*, $N_4H_{12}PtCl_2.PtCl_2$, isomeric with platosammonium chloride, and constituting the *green salt of Magnus*, the first discovered of the ammonia-platinum compounds. This last salt may also be prepared by passing sulphurous acid gas into a boiling solution of platinic chloride, till it is completely converted into platinous chloride (and is therefore no longer precipitated by sal-ammoniac), and neutralising the solution with ammonia. It forms dark green needles, insoluble in water, alcohol, and hydrochloric acid.

The *bromide* and *iodide* of this series are obtained by treating the solution of the sulphate with bromide or iodide of barium: they crystallise in cubes. The *oxide*, $N_4H_{12}PtO$, is obtained as a crystalline mass by decomposing the solution of the sulphate with an equivalent quantity of baryta-water, and evaporating the filtrate in a vacuum. It is strongly alkaline and caustic, like potash, absorbs carbonic acid rapidly from the air, and precipitates silver oxide from the solution of the nitrate. It is a strong base, neutralising acids completely, and expelling ammonia from its salts. It melts at 110°, giving off water and ammonia, and leaving platosammonium oxide. Its aqueous solution does not give off ammonia, even when boiled. The oxide absorbs carbon dioxide rapidly from the air, forming first a neutral carbonate, $N_4H_{12}PtCO_3.H_2O$, and afterwards an acid salt, $N_4H_{12}PtCO_3.H_2CO_3$. The *sulphate*, $N_4H_{12}PtSO_4$, and the *nitrate*, $N_4H_{12}Pt(NO_3)_2$, are obtained by decomposing the chloride with silver sulphate or nitrate; they are neutral, and crystallise easily.



5. *Platinammonium Compounds.*—The chloride, $Cl_2Pt{<}{NH_3Cl \atop NH_3Cl}$, is obtained by the action of chlorine on platosammonium chloride suspended in boiling water. It is a lemon-yellow crystalline powder, made up of quadratic octohedrons with truncated summits. It is insoluble in cold water, very slightly soluble in boiling water, or in water containing hydrochloric acid. It dissolves in ammonia at a boiling heat, and the solution, on cooling, deposits a yellow precipitate, consisting of platinodiammonium chloride. It dissolves in boiling potash without evolving ammonia.

Nitrates.—An *oxynitrate*, $N_2H_6Pt(NO_3)_2O$, is obtained by boiling the chloride, $N_2H_6PtCl_4$, for several hours with a dilute solution of silver nitrate. It is a yellow crystalline powder, sparingly soluble in cold, more soluble in boiling water. The *normal nitrate*, $N_2H_6Pt(NO_3)_4$, is obtained by dissolving the oxynitrate in nitric acid: it is yellowish, insoluble in cold water, soluble in hot nitric acid.

The *oxide*, $N_2H_3PtO_2$, is obtained by adding ammonia to a boiling solution of platinammonium nitrate; it is then precipitated in the form of a heavy, yellowish, crystalline powder, composed of small shining rhomboidal prisms; it is nearly insoluble in boiling water, and resists the action of boiling potash. Heated in a close vessel, it gives off water and ammonia, and leaves metallic platinum. It dis-

coloured powder, which detonat
but strongly when exposed to a g

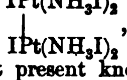
6. *Platinosemidiammoniu*

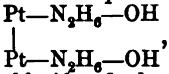
the preceding. The *chloride*, (
action of chlorine on platososemi
in yellow six-sided plates belongi
green at 100°, and dissolving
ammonia. A *basic nitrate*, $(OH)_2P$
amorphous yellow precipitate by
nitrate. A *chloronitrate*, $Cl_2Pt<$
of chlorine on platososemidiammo
yellow needles.

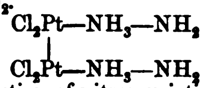
7. *Platinomonodiammoniu*
$Cl_2Pt<^{N_2H_6Cl}_{NH_3Cl}$, formed by the act
somonodiammonium chloride, crys
plates. A *bromonitrate*, $Br_2Pt<$
adding bromine to the nitrate of
yellow soluble crusts.

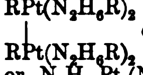
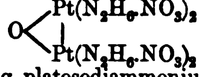
8. *Platinodiammonium* (
$PtCl_2<^{N_2H_6Cl}_{N_2H_6Cl}$, is obtained by pa
of platosodiammonium chloride;
chloride in ammonia, and expell
evaporation; or by precipitating
oxynitrate, or nitrato-chloride, wit

chloride, $Cl_2Pt\begin{matrix}<N_2H_6>\\ <N_2H_6>\end{matrix}SO_4$, formed by the action of sulphuric acid on the chloride, crystallises in slender transparent needles. An *oxalochloride*, $Cl_2Pt(N_2H_6)_2C_2O_4$, obtained by treating the chloride with ammonium oxalate, is a very soluble crystalline powder.

9. *Diplatinammonium Iodide*, 
$$\begin{matrix}IPt(NH_3I)_2\\ |\\ IPt(NH_3I)_2\end{matrix}$$
, or $I_2(Pt_2)^{vi}(NH_3I)_4$, the only term of this series at present known, is obtained by treating platosammonium iodide with boiling potash, and the resulting yellow powder with hydriodic acid. It is a black amorphous substance, which when again treated with potash and hydriodic acid yields the compound $I_2(Pt_4)^{x}(NH_3I)_8$, and this by similar treatment may be converted into the still more condensed compound $I_2(Pt_8)^{xviii}(NH_3I)_{16}$.

10. *Diplatosodiammonium Compounds.* — The *hydroxide*, 
$$\begin{matrix}Pt—N_2H_6—OH\\ |\\ Pt—N_2H_6—OH\end{matrix}$$
, formed by the action of caustic soda on the chloride of platososemidiammonium, is a greyish crystalline insoluble powder, which detonates violently when heated. Treated with hydrochloric acid, it yields a yellow powder, which is converted by boiling water into the *chloride*, $Pt_2(N_2H_6Cl)_2$.

11. *Diplatinodiammonium Chloride*, 
$$\begin{matrix}Cl_2Pt—NH_3—NH_2\\ |\\ Cl_2Pt—NH_3—NH_2\end{matrix}$$
, is a yellow amorphous powder formed by the action of nitromuriatic acid on the hydrate of the preceding series.

12. *Diplatino-tetradiammonium Compounds*, 
$$\begin{matrix}RPt(N_2H_6R)_2\\ |\\ RPt(N_2H_6R)_2\end{matrix}$$
or $N_8H_{24}Pt_2R_6$. An *oxynitrate*, 
$$O\begin{matrix}\diagup Pt(N_2H_6.NO_3)_2\\ |\\ \diagdown Pt(N_2H_6.NO_3)_2\end{matrix}$$
or $N_8H_{24}Pt_2(NO_3)_4O$, is produced by boiling platosodiammonium nitrate with nitric acid. It is a colourless, crystalline, detonating salt, slightly soluble in cold water, more soluble in boiling water, insoluble in nitric acid (Gerhardt). A *nitratoxychloride*, $N_8H_{24}Pt_2(NO_3)_4OCl_2$, discovered by Raewsky, is formed when Magnus's green salt is boiled with a large excess of nitric acid. Red fumes are then evolved, and the resulting solution deposits the nitrat-oxychloride in small brilliant needles, which deflagrate when heated, giving off water and sal-ammoniac, and leaving metallic platinum. The nitric acid in this salt may be replaced by an equivalent quantity of carbonic or oxalic acid, yielding the compounds, $N_8H_{24}Pt_2(CO_3)_2OCl_2$, and $N_8H_{24}Pt_2(C_2O_4)_2OCl_2$, both of which are crystallisable, and sparingly soluble. A *basic oxalonitrate*, $N_8H_{24}Pt_2(C_2O_4)_2(NO_3)_2O$, insoluble in water, is obtained by adding ammonium oxalate to the oxynitrate.

precipitates met

Platinic chloride and sodium
analytical investigations to dete
separate it from sodium. For th
are converted into chlorides, and
their weight of sodium platinochl
dissolved in a little water. Whe
appears complete, alcohol is adde
weighed filter, washed with w
weighed. The potassium chlorid
weight of the double salt; and t
the mixed chlorides employed, gi
difference; 100 parts of potassiu
30·51 parts of potassium chloride.

Capsules and crucibles of plat
chemist: the latter are constantl
fusing siliceous matter with alkal
injury in this operation, althou
corrodes the metal. The experim
to avoid introducing any oxide of a
lead or tin, into a platinum cruci
means occur, these metals will at
platinum, and the vessel will be
must never be put naked into a
placed within a covered earthen cr

PALLA

oxidable than platinum. When heated to redness in the air, especially in the state of sponge, it acquires a blue or purple superficial film of oxide, which is again reduced at a white heat. This metal is slowly attacked by nitric acid; its best solvent is nitro-muriatic acid.

Palladium, like platinum, forms two classes of compounds; namely, the palladious compounds, in which it is bivalent, and the palladic compounds, in which it is quadrivalent.

Chlorides.—The *dichloride*, or *Palladious chloride*, $PdCl_2$, is obtained by dissolving the metal in nitro-muriatic acid, and evaporating the solution to dryness. It is a dark-brown mass, which dissolves in water if the heat has not been too great, and forms double salts with many metallic chlorides. The palladio-chlorides of ammonium and potassium are much more soluble than the corresponding platinochlorides: they have a brownish-yellow tint.

The *tetrachloride*, or *Palladic chloride*, $PdCl_4$, exists only in solution and in combination with the alkaline chlorides. It is formed when the dichloride is digested in nitro-muriatic acid. The solution has an intense brown colour, and is decomposed by evaporation. Mixed with potassium chloride, or with sal-ammoniac, it gives rise to a red crystalline precipitate, which is but little soluble in water.

Palladious Iodide, PdI_2, is precipitated from the chloride or nitrate by soluble iodides, as a black mass, which gives off its iodine between 300° and 360°. Palladium-salts are employed for the quantitative estimation of iodine, chlorine and bromine not being precipitated by them.

Oxides.—The *monoxide*, or *Palladious oxide*, PdO, is obtained by evaporating to dryness, and cautiously heating the solution of palladium in nitric acid. It is black, and but little soluble in acids. The hydrate falls as a dark-brown precipitate when sodium carbonate is added to the above solution. It is decomposed by a strong heat.

The *dioxide*, or *Palladic oxide*, PdO_2, is not known in the separate state. From a solution of palladic chloride, alkalis and alkaline carbonates throw down a brown precipitate, consisting of hydrated palladic oxide combined with the alkali. This compound gives off half its oxygen at a moderate heat, and the whole at a higher temperature. From hot solutions a black precipitate is obtained, containing the anhydrous dioxide. The hydrate dissolves slowly in acids, forming yellow solutions. In strong hydrochloric acid it dissolves without decomposition, forming *potassio-palladic chloride*, arising from admixed potash; with dilute hydrochloric acid, on the contrary, it gives off chlorine.

Palladious Sulphide, PdS, is formed by fusing the metal with sulphur, or by precipitating a solution of a palladious salt with hydrogen sulphide. It is insoluble in ammonium sulphide.

200°. The yellow compound dissc
potash, forming a yellow solution, bu
even when the liquid is heated to
compound behaves in a similar man
converted into the yellow modificat
covered by Hugo Müller,* are analogo
and probably therefore in constitutio
the platinum compound, $N_2H_6PtCl_2$

pound being *palladiosemidiammonium*

and the yellow compound, *palladamm*

The yellow compound, digested with
palladammonium oxide, N_2H_6PdO, wh
water, having an alkaline taste and re
acid from the air. *Palladammonium su*
by the action of sulphurous acid o
crystallises in orange-yellow octohed
iodide, and *bromide* have likewise been

The *compound* $4NH_3.PdCl_2$, or
$Pd[NH_2(NH_4)Cl]_2$, separates from
palladammonium chloride in oblique

The *oxide*, $N_4H_{12}PdO$, obtained by
this chloride with silver oxide, is
crystallisable salts.

Palladious salts are well marked by
cipitate which they form with solution
sists of palladious cyanide, $PdCy_2$, and
spongy metal.

RHODIUM.

Atomic weight, 104·4. Symbol, R

THE solution from which platinum and palladium have been separated, in the manner already described, is mixed with hydrochloric acid, and evaporated to dryness. The residue is treated with alcohol, of specific gravity 0·837, which dissolves everything except the double chloride of rhodium and sodium. This is well washed with spirit, dried, heated to whiteness, and then boiled with water, whereby sodium chloride is dissolved out, and metallic rhodium remains. Thus obtained, rhodium is a white, coherent, spongy mass, still less fusible and less capable of being welded than platinum. Its specific gravity varies from 10·6 to 11.

Rhodium is very brittle: reduced to powder and heated in the air, it becomes oxidised, and the same alteration happens to a greater extent when it is fused with nitrate or bisulphate of potassium. None of the acids, singly or conjoined, dissolve this metal, unless it be in the state of alloy, as with platinum, in which state it is attacked by nitro-muriatic acid.

Rhodium forms but one chloride, containing $RhCl_3$, in which, like iron in ferric chloride, it may be regarded as either tri- or quadrivalent.

This chloride is prepared by adding silicofluoric acid to the double chloride of rhodium and potassium, evaporating the filtered solution to dryness, and dissolving the residue in water. It forms a brownish-red deliquescent mass, soluble in water, with a fine red colour. It is decomposed by heat into chlorine and metallic rhodium.

Rhodium and Potassium Chorides.—The salt, $RhCl_3.3KCl.3H_2O$, formed by mixing a solution of rhodic oxide in hydrochloric acid with a strong solution of potassium chloride, crystallises in sparingly soluble efflorescent prisms. Another double salt, containing $RhCl_3.2KCl.H_2O$, is prepared by heating in a stream of chlorine a mixture of equal parts of finely powdered metallic rhodium and potassium chloride. The salt has a fine red colour, is soluble in water, and crystallises in four-sided prisms. *Rhodium and sodium chloride*, $RhCl_3.3NaCl.12H_2O$, is also a very beautiful red salt, prepared like the last. The *ammonium salt*, $Rh_2Cl_6.6NH_4Cl.3H_2O$, obtained by decomposing the sodium salt with sal-ammoniac, crystallises in fine rhombohedral prisms.

Rhodium Oxides.—Rhodium forms four oxides, containing RhO, Rh_2O_3, RhO_2, and RhO_3.

The *monoxide*, RhO, is formed with incandescence, when the hydrated sesquioxide, $Rh_2O_3.3H_2O$, is heated in a platinum crucible. It is a dark grey substance, perfectly indifferent to acids.

The *sesquioxide*, or *Rhodic oxide*, Rh_2O_3, obtained by heating the

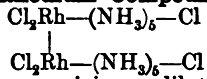
with nitric acid, to dissolve out the pota
insoluble in acids. When chlorine is
rhodic pentahydrate, $Rh_2O_3.5H_2O$, a blacl
tate of the trihydrate, $Rh_2O_3.3H_2O$, is forı
**pound gradually loses its gelatinous co
in colour, and is finally converted int
dioxide, $RhO_2.2H_2O$. The alkaline s
acquires a deep violet-blue colour.**

Trioxide, **RhO_3.—The blue alkaline
deposits, after a while, a blue powder,
and yielding, when treated with nitric
stance, consisting of the trioxide, easily**

**RHODIC SULPHATE, $Rh_2(SO_4)_3.12H_2O$,
sulphide with nitric acid, is a yellow
Potassio-rhodic sulphate, $RhK_3(SO_4)_3$, is
powder, formed by adding sulphuric aci
and potassium chloride.**

Ammoniacal Rhodium Compoun

$10NH_3.Rh_2Cl_6$, or



$$\begin{array}{l} Cl_2Rh—(NH_3)_5—Cl \\ \quad\;\; | \\ Cl_2Rh—(NH_3)_5—Cl \end{array}$$

**crystalline powder on mixing a dilut
ammonium chloride with excess of
filtered solution to evaporate. The co
Rh_2O_3, obtained by heating the chlor
strong base, from which the sulphate a
in crystalline form.**

Rhodic salts are, for the most part, r

IRIDIUM.

Atomic weight, 198. Symbol, Ir.

WHEN crude platinum is dissolved in nitromuriatic acid, a small quantity of a grey scaly metallic substance usually remains behind, having altogether resisted the action of the acid: this is a native alloy of iridium and osmium, called *osmiridium* or *iridosmine;* it is reduced to powder, mixed with an equal weight of dry sodium chloride, and heated to redness in a glass tube, through which a stream of moist chlorine gas is transmitted. The further extremity of the tube is connected with a receiver containing solution of ammonia. The gas, under these circumstances, is rapidly absorbed, iridium chloride and osmium chloride being produced: the former remains in combination with the sodium chloride; the latter, being a volatile substance, is carried forward into the receiver, where it is decomposed by the water into osmic and hydrochloric acids, which combine with the alkali. The contents of the tube when cold are treated with water, by which the iridium and sodium chloride is dissolved out; this is mixed with an excess of sodium carbonate, and evaporated to dryness. The residue is ignited in a crucible, boiled with water, and dried; it then consists of a mixture of ferric oxide and a combination of iridium oxide with soda: it is reduced by hydrogen at a high temperature, and treated successively with water and strong hydrochloric acid, by which the alkali and the iron are removed, while metallic iridium is left in a finely divided state. By strong pressure and exposure to a white heat, a certain degree of compactness may be communicated to the metal.*

Iridium is a white brittle metal, fusible with great difficulty before the oxy-hydrogen blowpipe. Deville and Debray, by means of their powerful oxy-hydrogen blast furnace, have fused it completely into a pure white mass, resembling polished steel, brittle in the cold, somewhat malleable at a red heat, and having a density equal to that of platinum, viz., 21·15. By moistening the pulverulent metal with a small quantity of water, pressing it tightly, first between filtering paper, then very forcibly in a press, and calcining it at a white heat in a forge fire, it may be obtained in the form of a compact, very hard mass, capable of taking a good polish, but still very porous, and of a density not exceeding 16·0. After strong ignition it is insoluble in all acids, but when reduced

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* Osmiridium, however, generally contains platinum, ruthenium, and other metals of the same group, which are not effectually separated by the method above described. The complete separation of the several metals of the platinum group has of late years formed the subject of several elaborate investigations, into which the limits of this work will not permit us to enter. (See Watts's Dictionary of Chemistry, iii. 35; iv. 241, 680; v. 101, 124.)

which it is also quadrivalent, a
to be incapable of uniting with n
element.* It forms also a trioxide
bably sexvalent.

Chlorides.—Iridium appears to
two of them—namely, the trichlori
obtained in definite form.

The *dichloride*, $IrCl_2$, is not kn
appears to exist in certain double sa

The *trichloride*, or *Iridious chlorid*
heating iridium with nitre, adding
saturate the alkali, warming the mi
precipitated hydrate of the sesquioxi
a dark yellowish-brown solution.
other metallic chlorides, forming cor
or *chloriridites*, which may be pre
sponding chloriridiates with sulphu
or potassium ferrocyanide. Claus
$IrCl_3.3NH_4Cl.3H_2O$, $IrCl_3.3KCl.3H$
They are olive-green pulverulent salt

The *tetrachloride*, or *Iridic chloride*,
dissolving very finely divided iridiu
trichloride, in nitromuriatic acid, a
boiling-point. On evaporating the s
of a black, deliquescent, amorphous
red colour at the edges; soluble, w
water. It unites with alkaline chlori
iridiochlorides or *chloriridiates*, anal
chloroplatinates. The *ammonium sa*
potassium salt. IrCl 2KCl

gently ignited and finely divided mixture of iridium with potassium chloride. It is soluble in boiling water, and crystallises in black octohedrons, yielding a red powder. The *sodium salt*, $IrCl_4.2NaCl.6H_2O$, prepared like the potassium salt, forms easily soluble black tables and prisms, isomorphous with the corresponding platinum salt.

Iodides.—Iridium forms three iodides, IrI_2, IrI_3, and IrI_4, analogous to the chlorides, and yielding similar double salts with the iodides of the alkali-metals.*

Oxides.—Iridium forms four oxides, IrO, Ir_2O_3, IrO_2, and IrO_3. The *monoxide*, or *hypoiridious oxide*, IrO, is but little known. It is obtained by precipitating an alkaline hypochloriridite with caustic alkali in an atmosphere of carbon dioxide; but on exposure to the air it is quickly converted into a higher oxide.

The *sesquioxide*, or *Iridious oxide*, Ir_2O_3, was formerly regarded as the most easily formed and most stable of the oxides of iridium; but, according to Claus, it has a great tendency to take up oxygen and pass to the state of dioxide. It may be prepared by gently igniting a mixture of potassium chloriridite ($IrCl_3KCl_3$) with sodium carbonate in an atmosphere of carbon dioxide; on treating the product with water, the sesquioxide remains in the form of a black powder insoluble in acids. It forms two hydrates, $Ir_2O_3.3H_2O$, and $Ir_2O_3.5H_2O$. It unites with bases, forming salts which may be called *iridites*. A solution of a chloriridite in excess of lime-water deposits, after standing for some time out of contact of air, a dirty yellow precipitate containing $3CaO.Ir_2O_3$.

The *dioxide*, or *Iridic oxide*, IrO_2, is, according to Claus, the most easily prepared and most stable of all the oxides of iridium, and is always deposited in the form of a bulky, indigo-coloured hydrate, $IrO_2.2H_2O$, when a solution of either of the chlorides of iridium or their double salts is boiled with an alkali; but it always retains 3 or 4 per cent. of the alkali. The hydrate may be obtained by dissolving the hydrated sesquioxide in potash and treating the solution with an acid. It dissolves in acids, forming solutions which are dark-brown when concentrated, reddish-yellow when dilute.

The *trioxide*, or *Periridic oxide*, IrO_3, is not known in the free state, but is formed in combination with potash, when iridium is fused for some time with nitre. The resulting blackish-green mass dissolves in water, forming a deep indigo-coloured solution of basic potassium periridiate, leaving a black crystalline powder consisting of acid periridiate.†

Iridium, like the other platinum metals, shows but little tendency to form oxygen salts. The oxides dissolve in acids, but no definite salts are obtained in this vay. The solution of iridic oxide in sulphuric acid has a dark-brown colour, which is not modified by

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* Offler, *Ueber die Iodverbindungen des Iridiums*. Göttingen, 1857.

† Claus, Ann. Ch. Pharm. lix. 249.

Sulphides.

to the first three oxides above described. *disulphide* are obtained as brown-black the solutions of the trichloride and tetracl hydrogen sulphide. The *monosulphide* is obtained by decomposing either of the hig vessel.

Ammoniacal Compounds of Iridium. *ammonium* and *iridosodiammonium*, Ir(NH_3 together with the corresponding sulphat platinous compounds of analogous compos semble in their properties. The *nitratochlo* is formed by heating the chloride, Ir (N acid. *Iridiodiammonium chloride*, Cl_2Ir[as a violet precipitate by treating the nit hydrochloric acid.*

The compound, $10NH_3.Ir_2Cl_6$, analogous above described (p. 522), but having no series, is obtained as a flesh-coloured cr longed digestion of ammonium chloririd ammonia. The corresponding carbonate, also been prepared. †

Iridic solutions (containing the dioxide dark brown-red colour; iridious solution oxide or trichloride) have an olive-green c an iridic solution are best observed with so other iridic compounds being but slightly

Iridic solutions give with *ammonium* o

RUTHENIUM.

Atomic weight, 104·4. Symbol, Ru.

THIS metal, discovered by Claus in 1846, occurs in platinum ore, and chiefly in osmiridium, of which there are two varieties—one scaly, consisting almost wholly of osmium, iridium, and ruthenium; while the other, which is granular, contains but mere traces of osmium and ruthenium, but is very rich in iridium and rhodium, To obtain ruthenium scaly osmiridium is heated to bright redness in a porcelain tube, through which a current of air (freed from carbonic acid by passing through potash, and from organic matter by passing through oil of vitriol), is drawn by means of an aspirator. The osmium and ruthenium are thereby oxidised, the former being carried forward as tetroxide and condensed in caustic potash solution, while the ruthenium oxide remains behind, together with iridium; and by fusing this residue with potassium hydroxide, treating the mass with water, and leaving the liquid in a corked bottle for about two hours to clarify, an orange-coloured solution of potassium rutheniate is obtained, which, when neutralised with nitric acid, deposits velvet-black ruthenium sesquioxide, and this, when washed, dried, and ignited in hydrogen, yields the metal.

Ruthenium, thus prepared, forms porous lumps very much like iridium, and is moderately easy to pulverise. It is the most refractory of all metals except osmium. Deville and Debray have, however, fused it by placing it in the hottest part of the oxyhydrogen flame. After fusion it has a density of 11·4; that of the porous metal is 8·6.

Ruthenium is scarcely attacked by nitromuriatic acid. It is, however, more easily oxidised than platinum, or even than silver. When pure it is easily oxidised by fusion with potassium hydroxide, still more easily on addition of a small quantity of nitrate or chlorate, producing potassium rutheniate, which dissolves in water with orange-yellow colour.

Chlorides.—Ruthenium forms three chlorides, $RuCl_2$, $RuCl_3$, and $RuCl_4$.

The *dichloride*, $RuCl_2$, is produced, together with the trichloride, by igniting pulverised ruthenium in a stream of chlorine, the trichloride then volatilising, while the dichloride remains in the form of a black crystalline powder, insoluble in water and in all acids, even nitro-muriatic acid, and only partially decomposed by alkalis. A soluble dichloride is formed by passing sulphydric acid gas into a solution of the trichloride, a brown sulphide being then precipitated, and the solution acquiring a fine blue colour.

The *trichloride*, or *Ruthenious chloride*, $RuCl_3$, prepared by precipitating a solution of potassic rutheniate with an acid, dissolving the precipitated black oxide in hydrochloric acid, and evaporating, is a yellow-brown, crystalline, very deliquescent mass, becoming

a solution of ruthenic hydrate in hydroc
chloride, and evaporating to the crystall
with rose-coloured iridescence, very solu
in alcohol. The *ammonium salt*, $RuCl_4$
the potassium salt, which it resembles cl

Oxides.—Ruthenium forms five oxide
RuO_3, and RuO_4, the fourth, however, b
bination.

The *monoxide*, RuO, obtained by calc
sodium carbonate in a current of carbon
residue with water, has a dark-grey col
not acted upon by acids; but is reduce
temperatures.—The *sesquioxide*, or *Rut*
bluish-black powder, formed by heating
corresponding hydrate, $Ru_2O_3.3H_2O$, or
cipitating ruthenious chloride with an
blackish-brown substance which dissol
acids.—The *dioxide*, or *Ruthenic oxide*, R
obtained by roasting the disulphide. *R*
or RuH_4O_4, is obtained as a gelatinous
potassium chlororutheniate with sodiu
RuO_3, commonly called *ruthenic acid*, is
salt, which is obtained by igniting rut
and nitre: it forms an orange-yello
RuO_4, is a volatile compound, analogous
by heating ruthenium with potash and
dissolving the fused mass in water, an
the solution in a tubulated retort, con
with a receiver containing potash. Th
in the neck of the retort

Ru_2S_3. When hydrogen sulphide is passed for a long time into a solution of the trichloride, ruthenium disulphide, RuS_2, is formed, as a brown-yellow precipitate, becoming dark-brown by calcination.

Ammoniacal Ruthenium Compounds.—*Tetrammonio-hyporuthenious Chloride*, $4NH_3.RuCl_2.3H_2O$ or $Ru[NH_2(NH_4)Cl]_2.3H_2O$, is formed by boiling the solution of ammonium chlororutheniate ($RuCl_4.2NH_4Cl$) with ammonia. It forms golden-yellow oblique rhombic crystals, very soluble in water, insoluble in alcohol. Treated with silver oxide, it yields the corresponding oxide, $4NH_3RuO$, which, however, is decomposed by evaporation of its solution, giving off half its ammonia, and leaving the compound, $2NH_3.RuO$. The carbonate, nitrate, and sulphate, obtained by treating this last-mentioned oxide with the corresponding silver salts, form yellow crystals.

The compounds of ruthenium may readily be distinguished from those of the other platinum-metals, by fusing a few milligrams of the substance in a platinum spoon, with a large excess of nitre, leaving it to cool when it ceases to froth, and dissolving the cooled mass in a little distilled water. An orange-yellow solution of potassium rutheniate is thus formed, which on addition of a drop or two of nitric acid, yields a bulky, black precipitate; and on adding hydrochloric acid to the liquid, with the precipitate still in it, and heating it in a porcelain crucible, the oxide dissolves, forming a solution which has a fine orange-yellow colour when concentrated, and when treated with *hydrogen sulphide*, till it becomes nearly black, yields a filtrate of a splendid sky-blue colour. Characteristic reactions are also obtained with *potassium sulphocyanate*, which colours the liquid deep red, changing to violet on heating, and with *lead acetate*, which forms a purple-red precipitate.

OSMIUM.

Atomic weight, 199·2. Symbol, Os.

THE separation of this metal from iridium, ruthenium, and the other metals with which it is associated in native osmiridium, and in platinum residues, depends chiefly on its ready oxidation with nitric or nitromuriatic acid, or by ignition in air or oxygen, and the volatility of the oxide thus produced.

To prepare metallic osmium, the solution obtained by condensing the vapour of osmium tetroxide in potash (p. 527) is mixed with excess of hydrochloric acid, and digested with mercury in a well-closed bottle at 40°. The osmium is then reduced by the mercury, and an amalgam is formed, which, when distilled in a stream of

metallic lustre, ...
igniting precipitated osmium sulphide n
the melting heat of nickel, obtained i
divisible lumps. When heated to the m
becomes more compact, and acquires a d
a still higher temperature, capable of melt
and volatilising platinum, osmium lik
does not melt; in fact, it is the most refi

Osmium in the finely divided state i
tinuing to burn when set on fire, till it is
In this state also it is easily oxidised
acid, being converted into tetroxide. B
heat, it becomes less combustible, anc
or nitromuriatic acid. Osmium which
melting point of rhodium, does not give
when heated in the air to the melting p
higher temperatures.

Osmium Chlorides.—Osmium form
to those of iridium and ruthenium.
chlorine gas, there is formed, first a b
dichloride, then a red sublimate of the te
or *hypo-osmious chloride*, dissolves in
colour. It is likewise formed by the
either of the higher chlorides, into wh
easily converted by oxidation. The a
renders it more stable, by forming a d
$OsCl_3$, has not been isolated, but is c
tained by treating the sesquioxide
forms double salts with alkaline ch
$OsCl_3.3KCl.3H_2O$, is produced, toget

forming salts sometimes called osmiochlorides, or chlorosmates. From the solutions of these salts, *hydrogen sulphide* and *ammonium sulphide* slowly precipitate a yellow-brown sulphide, insoluble in alkaline sulphides; *silver nitrate* forms an olive-green; *stannous chloride*, a brown precipitate. *Tannic acid*, on heating, produces a blue colour, but no precipitate; *potassium ferrocyanide*, first a green, then a blue colour; *potassium iodide*, a deep purple-red colour. *Potash* gives a black, *ammonia* a brown precipitate, slowly in the cold, immediately on boiling. Metallic *zinc* and *sodium formate* throw down metallic osmium.

Sodium osmiochloride, $OsCl_4.2NaCl$, prepared by heating a mixture of osmium sulphide and sodium chloride in a current of chlorine, crystallises in orange-coloured rhombic prisms, an inch long, easily soluble in water and in alcohol. The *potassium* and *ammonium salts*, of analogous composition, are obtained as red-brown crystalline precipitates on adding sal-ammoniac or potassium chloride to the solution of the sodium salt.

Oxides. — Osmium forms five oxides analogous to those of ruthenium. The *monoxide*, or *hypo-osmious oxide*, OsO, is obtained by igniting hypo-osmious sulphite in a stream of carbonic acid gas; also as a blue-black hydrate, by heating the same salt with strong potash solution in a closed vessel. *Hypo-osmious sulphite*, $OsSO_3$ or $OsO.SO_2$, is a black-blue salt, produced by mixing the aqueous solution of osmium tetroxide with sulphurous acid.—The *sesquioxide* or *osmious oxide*, Os_2O_3, is obtained by heating either of the double salts of the trichloride with sodium carbonate in a stream of carbonic acid gas. It is a black powder, insoluble in acids. The *hydrate*, obtained by precipitation, has a dirty brown-red colour, is soluble in acids, but does not yield pure salts.

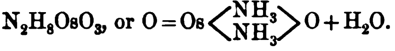
The *dioxide*, or *Osmic oxide*, OsO_2, is obtained as a black insoluble powder, by heating potassium osmiochloride with sodium carbonate in a stream of carbonic acid gas, or in copper-red metallic shining lumps, by heating the corresponding hydrate. *Osmic hydrate*, $OsO_2.2H_2O$, is obtained by precipitating a solution of potassium osmio-chloride with potash, at the boiling heat, or in greater purity by mixing a solution of potassic osmite, $K_2O.OsO_3$, with dilute nitric acid.

The *trioxide*, OsO_3, is not known in the free state, but combines with alkalis, forming salts called osmites, which are produced by the action of reducing agents on the tetroxide in presence of alkalis. The *potassium salt*, $K_2O.OsO_3.2H_2O$, is a rose-coloured crystalline powder.

The *tetroxide*, OsO_4, commonly called *osmic acid*, is the volatile, strong-smelling compound, formed when osmium or either of its lower oxides is heated in the air, or treated with nitric or nitro-muriatic acid. It may be prepared by heating osmium in a current of oxygen gas, and condenses in the cool part of the apparatus in colourless, transparent crystals. It melts below 100°, and boils at off the tetroxide

Sulphides.—Osmium burns in sulph
of osmium are said to exist, analogous t
being produced by decomposing the co
hydrogen sulphide, and the tetrasulphid
solution of the tetroxide. The last i
soluble in water, whereas the others
soluble in water, and forming deep yello

Ammoniacal Osmium Compounds
sium osmite, mixed with sal-ammoniac,
precipitate, consisting, according to Cl
nium chloride, $Os(NH_3Cl)_2$. An aqueo
treated with ammonia, yields a brown-



$$N_2H_8OsO_3, \text{ or } O=Os\left\langle\begin{matrix}NH_3\\NH_3\end{matrix}\right\rangle O + H_2O.$$

OSMIAMIC ACID, $H_2Os_2N_2O_5$.—The p
acid, $K_2Os_2N_2O_5$, is produced by the a
solution of osmium tetroxide in excess

$$6OsO_4 + 8NH_3 + 6KHO = 3K_2O$$

It separates as a yellow crystalline
treated with silver nitrate, yields a pre
$Ag_2Os_2N_2O_5$, from which the aqueou
decomposition with hydrochloric acid.
posing, not only the carbonates, but al
and sodium. The osmiamates of th
earth-metals are soluble in water; t
salts are insoluble.

APPENDIX.

HYDROMETER TABLES.

TABLE I.—COMPARISON OF THE DEGREES OF BAUMÉ'S HYDROMETER WITH THE REAL SPECIFIC GRAVITIES.

For Liquids Heavier than Water.

Degrees.	Specific Gravity.	Degrees.	Specific Gravity.	Degrees.	Specific Gravity.
0	1·000	26	1·206	52	1·520
1	1·007	27	1·216	53	1·535
2	1·013	28	1·225	54	1·551
3	1·020	29	1·235	55	1·567
4	1·027	30	1·245	56	1·583
5	1·034	31	1·256	57	1·600
6	1·041	32	1·267	58	1·617
7	1·048	33	1·277	59	1·634
8	1·056	34	1·288	60	1·652
9	1·063	35	1·299	61	1·670
10	1·070	36	1·310	62	1·689
11	1·078	37	1·321	63	1·708
12	1·085	38	1·333	64	1·727
13	1·094	39	1·345	65	1·747
14	1·101	40	1·357	66	1·767
15	1·109	41	1·369	67	1·788
16	1·118	42	1·381	68	1·809
17	1·126	43	1·395	69	1·831
18	1·134	44	1·407	70	1·854
19	1·143	45	1·420	71	1·877
20	1·152	46	1·434	72	1·900
21	1·160	47	1·448	73	1·924
22	1·169	48	1·462	74	1·949
23	1·178	49	1·476	75	1·974
24	1·188	50	1·490	76	2·000
25	1·197	51	1·495		

TABLE II.

Baumé's Hydrometer for Liquids Lighter than Water.

Degrees.	Specific Gravity.	Degrees.	Specific Gravity.	Degrees.	Specific Gravity.
10	1·000	27	0·896	44	0·811
11	0·993	28	0·890	45	0·807
12	0·986	29	0·885	46	0·802
13	0·980	30	0·880	47	0·798
14	0·973	31	0·874	48	0·794
15	0·967	32	0·869	49	0·789
16	0·960	33	0·864	50	0·785
17	0·954	34	0·859	51	0·781
18	0·948	35	0·854	52	0·777
19	0·942	36	0·849	53	0·773
20	0·936	37	0·844	54	0·768
21	0·930	38	0·839	55	0·764
22	0·924	39	0·834	56	0·760
23	0·918	40	0·830	57	0·757
24	0·913	41	0·825	58	0.753
25	0·907	42	0·820	59	0·749
26	0·901	43	0·816	60	0·745

These two tables are on the authority of Francœur: they are taken form the *Handwörterbuch der Chemie* of Liebig, Poggendorff and Wöhler. Baumé's hydrometer is very commonly used on the Continent, especially for liquids heavier than water. For lighter liquids the hydrometer of Cartier is often employed in France. Cartier's degrees differ but little from those of Baumé.

In the United Kingdom, Twaddell's hydrometer is a good deal used for dense liquids. This instrument is so graduated that the real specific gravity can be deduced by an extremely simple method from the degree of the hydrometer; namely, by multiplying the latter by 5, and adding 1000; the sum is the specific gravity, water being 1000. Thus 10, Twaddell indicates a specific gravity of 1050, or 1·05; 90° Twaddell, 1450, or 1·45.

In the Customs and Excise, Sikes's hydrometer is used.

TABLE III.

ABSTRACT

OF REGNAULT'S TABLE OF THE MAXIMUM TENSION OF WATER-VAPOUR, AT DIFFERENT TEMPERATURES, EXPRESSED IN MILLIMETERS OF MERCURY.

Temperature.	Tension, millimeters.	Temperature.	Tension, millimeters.
− 32° C.	0·320	100° C.	760·000
30	0·386	105	906·410
25	0·605	110	1075·370
20	0·927	115	1269·410
15	1·400	120	1491·280
10	2·093	125	1743·880
5	3·113	130	2030·280
0	4·600	135	2353·730
+ 5	6·534	140	2717·630
10	9·165	145	3125·55
15	12·699	150	3581·23
20	17·391	155	4088·56
25	23·550	160	4651·62
30	31·548	165	5274·54
35	41·827	170	5961·66
40	54·906	175	6717·43
45	71·391	180	7546·39
50	91·982	185	8453·23
55	117·478	190	9442·70
60	148·791	195	10519·63
65	186·945	200	11688·96
70	233·093	205	12955·66
75	288·517	210	14324·80
80	354·643	215	15801·33
85	433·041	220	17390·36
90	525·450	225	19097·04
95	633·778	230	20926·40

TABLE IV.

WEIGHTS AND MEASURES.

480 grains Troy = 1 oz. Troy.
437·5 ,, = 1 oz. Avoirdupois.
7000 ,, = 1 lb. Avoirdupois.
5760 ,, = 1 lb. Troy.

The imperial gallon contains of water at 62° F. ($16\frac{2}{3}$° C.) 70,000 grains.
The pint ($\frac{1}{8}$ of gallon) . . . . . . 8,750 ,,
The fluid ounce ($\frac{1}{20}$ of pint) . . . . . 437·5 ,,

The pint equals 34·56 cubic inches.

TABLE V.

COMPARISON OF FRENCH AND ENGLISH MEASURES. BY DR. WARREN DE LA RUE.

MEASURES OF LENGTH.

	In English Inches.	In English Feet = 12 Inches.	In English Yards = 3 Feet.	In English Fathoms = 6 Feet.	In English Miles = 1,760 Yards.
Millimeter	0·03937	0·0032809	0·0010936	0·0005468	0·0000006
Centimeter	0·39371	0·0328090	0·0109363	0·0054682	0·0000062
Decimeter	3·93708	0·3280899	0·1093633	0·0546816	0·0000621
Meter	39·37079	3·2808992	1·0936331	0·5468165	0·0006214
Decameter	393·70790	32·8089920	10·9363310	5·4681655	0·0062138
Hectometer	3937·07900	328·0899200	109·3633100	54·6816550	0·0621382
Kilometer	39370·79000	3280·8992000	1093·6331000	546·8165500	0·6213824
Myriameter	393707·900000	32808·9920000	10936·3310000	5468·1655000	6·2138244

1 Inch = 2·539954 Centimeters.
1 Foot = 3·0479449 Decimeters.

1 Yard = 0·91438348 Meter.
1 Mile = 1·6093149 Kilometer.

MEASURES OF SURFACE.

	In English Square Feet.	In English Sq. Yards = 9 Square Feet.	In English Poles = 272·25 Sq. Feet.	In English Roods = 10,890 Sq. Feet.	In English Acres = 43,560 Sq. Feet.
Contiare or square meter	10·7642993	1·1960333	0·0395383	0·000988457	0·0002471143
Are or 100 square meters	1076·4299342	119·6033260	3·9538290	0·098845724	0·0247114310
Hectare or 10,000 sq. meters	107642·9934183	11960·3326020	395·3828959	9·884572398	2·4711430996

1 Square Inch = 6·4513669 Square Centimeters.
1 Square Foot = 9·2899683 Square Decimeters.

1 Square Yard = 0·83609715 Square Meter or Centiare.
1 Acre = 0·404671021 Hectare.

TABLE V. (*Continued*).

MEASURES OF CAPACITY.

	In Cubic Inches.	In Cubic Feet =1,728 Cubic Inches.	In Pints =34·65923 Cubic Inches.	In Gallons = 8 Pints=277·27384 Cubic Inches.	In Bushels=8 Gallons=2218·19075 Cubic Inches.
Millilitre, or Cubic Centimeter . .	0·061027	0·0000353	0·001761	0·90022010	0·000027512
Centilitre, or 10 Cubic Centimeters .	0·610271	0·0003532	0·017608	0·00220097	0·000275121
Decilitre, or 100 Cubic Centimeters .	6·102705	0·0035317	0·176077	0·02200967	0·002751208
Litre, or Cubic Decimeter . . .	61·027052	0·0353166	1·760773	0·22009668	0·027512085
Decalitre, or Centistere	610·270515	0·3531658	17·607734	2·20096677	0·275120846
Hectolitre, or Decistere	6102·705152	3·5316581	176·077341	22·00966767	2·751208459
Kilolitre, or Stere or Cubic Meter .	61027·051519	35·3165807	1760·773414	220·09667675	27·512084594
Myrialitre, or Decastere	610270·515194	353·1658074	17607·734140	2200·96676750	275·120845937

1 Cubic Inch = 16·3861759 Cubic Centimeters. 1 Cubic Foot = 28·3153119 Cubic Decimeters. 1 Gallon = 4·543457969 Litres.

MEASURES OF WEIGHT.

	In English Grains.	In Troy Ounces = 480 Grains.	In Avoirdupois lbs. = 7,000 Grains.	In Cwts.=112 lbs. =784,000 Grains.	Tons = 20 Cwts. = 15,680,000 Grains.
Milligram	0·015432	0·000032	0·0000022	0·00000002	0·000000001
Centigram	0·154323	0·000322	0·0000220	0·00000020	0·000000010
Decigram	1·543235	0·003215	0·0002205	0·00000197	0·000000098
Gram	15·432349	0·032151	0·0022046	0·00001968	0·000000984
Decagram	154·323488	0·321507	0·0220462	0·00019684	0·000009842
Hectogram	1543·234880	3·215073	0·2204621	0·00196841	0·000098421
Kilogram	15432·348800	32·150727	2·2046213	8·01968412	0·000984206
Myriagram	154323·488000	321·507267	22·0462126	0·19684118	0·009842059

1 Grain = 0·064798950 Gram. 1 Troy oz. = 31·103496 Gram. 1 lb. Avd. = 0·45359265 Kilogr. 1 Cwt. = 50·80237689 Kilog.

TABLE VI.

FOR CONVERTING DEGREES OF THE CENTIGRADE THERMOMETER INTO DEGREES OF FAHRENHEIT'S SCALE.

Centigrade.	Fahrenheit.	Centigrade.	Fahrenheit.	Centigrade.	Fahrenheit.
− 90°	− 130°	− 60°	− 76°	− 30°	− 22°
85	121	55	67	25	13
80	112	50	58	20	4
75	103	45	49	15	+ 5
70	94	40	40	10	14
65	85	35	31	5	23
0°	+ 32°	+ 100°	+ 212°	+ 200°	+ 392°
+ 5	41	105	221	205	401
10	50	110	230	210	410
15	59	115	239	215	419
20	68	120	248	220	428
25	77	125	257	225	437
30	86	130	266	230	446
35	95	135	275	235	455
40	104	140	284	240	464
45	113	145	293	245	473
50	122	150	302	250	482
55	131	155	311	255	491
60	140	160	320	260	500
65	149	165	329	265	509
70	158	170	338	270	518
75	167	175	347	275	527
80	176	180	356	280	536
85	185	185	365	285	545
90	194	190	374	290	554
95	203	195	383	295	563

1°C. = 1·8° F.
2 = 3·6
3 = 5·4
4 = 7·2

TABLE VII.

WEIGHT OF ONE CUBIC CENTIMETER OF ATMOSPHERIC AIR, IN GRAMS, AT DIFFERENT TEMPERATURES, FOR EVERY 5 DEGREES FROM 0 TO 300° C. AT 760 MM.

		Difference.			Difference.
0°	0·001293	23	155°	0·000824	9
5	0·001270	22	160	0·000815	9
10	0·001248	22	165	0·000806	9
15	0·001226	21	170	0·000797	9
20	0·001205	20	175	0·000788	9
25	0·001185	20	180	0·000779	9
30	0·001165	19	185	0·000770	8
35	0·001146	18	190	0·000762	8
40	0·001128	17	195	0·000754	8
45	0·001111	17	200	0·000746	8
50	0·001094	17	205	0·000738	8
55	0·001077	17	210	0·000730	8
60	0·001060	16	215	0·000722	7
65	0·001044	15	220	0·000715	7
70	0·001029	15	225	0·000708	7
75	0·001014	14	230	0·000701	7
80	0·001000	14	235	0·000694	7
85	0·000986	14	240	0·000687	7
90	0·000972	13	245	0·000680	6
95	0·000959	13	250	0·000674	6
100	0·000946	13	255	0·000668	6
105	0·000933	12	260	0·000662	6
110	0·000921	12	265	0·000656	6
115	0·000909	11	270	0·000650	6
120	0·000898	11	275	0·000644	6
125	0·000887	11	280	0·000638	6
130	0·000876	11	285	0·000632	6
135	0·000865	11	290	0·000626	5
140	0·000854	10	295	0·000621	5
145	0·000844	10	300	0·000616	
150	0·000834				

The column of Differences is intended to facilitate the calculation of the intermediate values. Thus to find the weight of 1 cub. cent. of air for 52°, we must add to the weight for 50°, two-fifths of the difference (17) between this and the number for 55 degrees: thus

Weight of 1 cub. cent. of air at 50° = 0·001094
Add $\frac{2}{5}$ of 17 = 7
Weight of 1 cub. cent. of air at 55° = 0·01101.

TABLE VIII.

FOR THE CALCULATION OF $\frac{1}{1+0{\cdot}00367\,t}$. (*See page* 58).

t		*t*		*t*		*t*		*t*	
1	0·99634	31	0·89785	61	0·81708	91	0·74964	121	0·69249
2	0·99271	32	0·89490	62	0·81464	92	0·74758	122	0·69073
3	0·98911	33	0·89197	63	0·81221	93	0·74554	123	0·68899
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ERRATA.

Page 55, line 9 from bottom, *for* each degree *read* every 5 degrees.
,, 338, ,, 6 ,, ,, alkalis ,, alkali.
,, 349, ,, 2 from top, ,, tronai ,, trona.
,, 265, column 5, line 6 of Table, *for* Si ,, Se.

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